This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

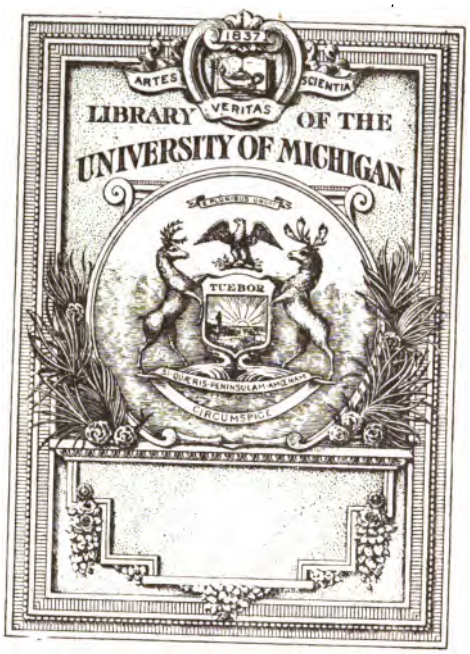
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`



THE GIFT OF
Prof. C. D. Campbell

QD
101
.W116
1913

E. D. Campbell.

QUANTITATIVE ANALYSIS IN PRACTICE

QUANTITATIVE ANALYSIS IN PRACTICE

AN INTRODUCTORY COURSE DESIGNED FOR COLLEGES AND UNIVERSITIES

BY

JOHN WADDELL

B.A. (DALHOUSIE UNIVERSITY), B.Sc. (LONDON), PH.D. (HEIDELBERG), D.Sc. (EDINBURGH), FORMERLY ASSISTANT TO THE PROFESSOR OF CHEMISTRY IN EDINBURGH, ASSISTANT PROFESSOR OF CHEMISTRY SCHOOL OF MINING (QUEEN'S UNIVERSITY), KINGSTON, CANADA

PHILADELPHIA

P. BLAKISTON'S SON & CO.

1012 WALNUT STREET

1913

Printed in Great Britain.

L 28

PREFACE

I OFFER no apology for adding another to the already fairly long list of books upon Quantitative Analysis. If my book is without merit, it will doubtless soon attain the oblivion which it deserves; but if it really fills a want, as I am encouraged by Sir William Crookes to believe that it does, I trust that it will commend itself to many teachers, students and analysts.

The book is intended as an introductory course. There are a number of the more common determinations, and the variety is such that it gives a choice which will, I trust, meet the needs of different classes of students.

There are several features in the book which, I hope, will be considered to increase its usefulness, two or three of which I shall mention. One is the endeavour that I have made to connect analytical processes with the general properties of the substances concerned. An illustration of what I mean will be found in the discussion of the precipitation of magnesium ammonium phosphate, and what happens on its ignition.

Another feature is the care taken to show how far the details of an operation may affect, on the one hand, the accuracy, and on the other hand, the speed of an analysis.

A third feature is the attempt to give the student some idea of the time required for the various operations and analysis. Almost all students, in looking back on a year's work, realise that much time was wasted, and that the waste of time was largely due to their lack of knowledge of the amount of work that might reasonably be expected of them in the time allotted. I am not aware of any book on analysis which attempts to set a standard of speed as I have done. Such a standard cannot, of course, be exact; it gives the student some idea, however, of what he should be able to do.

The directions for the carrying out of the different operations are full and explicit, and the reasons for the particular precautions are dealt with, as well as the general principles under-

327976

lying the processes. Any teacher who takes the trouble to question his students sufficiently knows how liable they are to fail in understanding just what they are doing. The method that I have adopted in this book is due to a lengthened experience of the difficulties confronting the student in beginning Quantitative Analysis.

Among those to whom I am indebted for criticisms and suggestions, I wish to mention specially Prof. J. Watson Bain, of Toronto University, and Prof. Eben. MacKay, of Dalhousie University.

I desire also to thank Mr. J. A. McRae, M.A., A.I.C., of Queen's University, for very kindly reading all of the proof and preparing the Index.

JOHN WADDELL.

September, 1913.

CONTENTS

CHAPTER		PAGE
I.	Introduction	1
II.	General Methods of Analysis	5
III.	General Directions regarding Work	9
IV.	Course of Analysis	12
V.	Barium Chloride	37
VI.	Magnesium Sulphate	44
VII.	Calcium Carbonate	55
VIII.	Cement, Limestone, Clay	61
IX.	Coal	73
X.	Copper	77
XI.	Alkalimetry and Acidimetry	83
XII.	Chlorimetry. Bleaching Powder	94
XIII.	Iron Ore	98
XIV.	Water	108
XV.	Iron and Steel	114
XVI.	Lead Ore	124
XVII.	Nickel and Cobalt Ore	131
XVIII.	Zinc Ore	134
XIX.	Bronze	137
Appendix A.	The Balance and Weights	145
„ B.	Calibration of Flasks, Pipettes and Burettes	147
„ C.	Electrolytic Dissociation and the Mass Law	149
„ D.	Analytical Factors	154
„ E.	Logarithms	156
Index		161

QUANTITATIVE ANALYSIS IN PRACTICE

CHAPTER I

INTRODUCTION

In Quantitative Analysis, two things, honesty and accuracy, are essential, while one, speed, is very important.

1. **HONESTY.**—A text-book on analysis is not intended to inculcate honesty, but a word or two may be said on the subject. Common honesty on the part of the analyst is assumed; an example will serve to illustrate what may be called chemical or scientific honesty.

The amount of lime in pure calcium carbonate is 56 per cent. If on analysis a result 55·80 per cent. is obtained, and a little is known to have been lost, that small amount is liable to be regarded as making up the difference. If, however, the result obtained is 56·20 per cent., the tendency is to forget that some was lost or to consider it inappreciable, and to say that the error is only 0·2 per cent., whereas it is really greater, and honesty requires one to admit that one's analysis is not so good as it seems. Honesty on the part of the student reporting his results to an instructor involves that his record book should show the error impartially in each case.

Very frequently the beginner, if he knows that he has made a slight error in some part of the operation and finds that his results are wrong, assumes that the error noticed would account for the mistake and considers the rest of his work well done, whereas the error he has made might have actually brought his results nearer to the theoretical than they would otherwise have been, and, therefore, his work is correspondingly worse. For instance, if the amount of iron in an iron ore is found to be

too low, and it is known that in the standardising of the potassium permanganate used, some of the Mohr's salt was lost, the student will too readily assume that the mistake is accounted for, though the fact is exactly the reverse. Care should always be taken that one does not give oneself credit for better work than has been done.

2. **ACCURACY.**—*Absolute* accuracy is not to be attained. In the analytical laboratories of the Geological Survey Department, two of the good analysts might determine a dozen different substances in a rock of complicated composition and might differ by only a few hundredths of a per cent. in the quantity of each constituent, but accuracy of that kind cannot be expected of the student in the ordinary laboratory. Quite apart from the errors due to poor manipulation, errors may be due to the imperfection of the methods used. No mode of separation is absolutely accurate, no precipitate is perfectly insoluble. Errors are to be met at every turn. What is meant by saying that accuracy is essential is, that the analyst should strive to make his work accurate within the limits of error of the method. The requisite accuracy depends partly on the thing determined. In some cases, as, for instance, the determination of phosphorus in steel, an error greater than a few thousandths of 1 per cent. will render the analysis useless. A law-suit might arise over the question whether a certain steel contains twenty-thousandths or forty-thousandths of 1 per cent. of phosphorus. In some other determinations, such as that of copper, duplicate analyses should agree within a few hundredths of a per cent., while in some cases, like the chlorine in barium chloride, there may be a difference of one or two tenths of a per cent. The difference in the degree of accuracy is not, however, so great as may appear from the above figures, because the total phosphorus in steel is very small, and a copper ore may be of low grade, whereas the percentage of chlorine in barium chloride is nearly 30, and an error of two-tenths is one part in 150.

3. **SPEED.**—The relative value of speed and accuracy differs under different conditions. In a metallurgical or manufacturing establishment, it may be of great service to know the quantity of a particular constituent accurately to $\frac{1}{2}$ per cent.

within a few *minutes*, whereas to know it to within one-tenth of a per cent. within a few hours would be valueless. In an ironworks, many determinations are made daily to check the character and amounts of ore and flux, and unless the information is obtained at the proper time the occasion will be past. For the student, however, speed is quite subservient to accuracy, but every effort should be made to increase the speed while not diminishing the accuracy. If an analysis which should take only six hours takes twelve, there is evidently a great waste of time. Some of the instructions given in this book are intended to aid in the attainment of accuracy, and some to help in increasing speed.

Speed may be gained, either by attention to details in the particular process, or by arranging the work, so that the various operations fit into each other without loss of time. Filtration is made more rapid by having the filter properly fitted to the funnel, by having the liquid hot, and by maintaining the level of the liquid in the funnel. This provides an example of the first method for increasing speed. The second method may be illustrated by the determination of the water of crystallisation in barium chloride, and of barium in the same salt. A platinum crucible is required in both operations, but for the barium, there are the preliminary operations of precipitation and filtration, and during this time the crucible would be idle, so far as this determination is concerned, and it may readily be used for heating another portion of the salt in order to determine the water. Another instance may be given. A student frequently plans to ignite a precipitate at the beginning of a laboratory period, and finds that his crucible needs to be cleaned and heated before he can do so. The crucible must, of course, be cooled in the desiccator before weighing, and the time required may be twenty minutes or more. If two or three minutes had been used at the end of the previous laboratory period for cleaning and heating the crucible, it could have remained in the desiccator in the meantime without harm, and have been ready to weigh at the very beginning of the new day's work, and the ignition could have been proceeded with without loss of time.

A little foresight will save many a minute, and in the course of the year many an hour. In this connection, the student

cannot be too strongly urged to read carefully the description of the whole process before beginning a determination, so that he may thoroughly understand the reason for what he is doing. There is a possible exception to this rule. If the first steps of an operation are so plain that no mistake can be made, it may sometimes be advisable to simply follow the directions for this part of the operation, in case the end of the laboratory period is near and there is no time to read the whole description. Under such circumstances, the whole process should be studied before the next attendance.

It happens, not infrequently, that the first stages of a determination require time for evaporation, and before a student has quite finished one determination it may be advisable for him to read the description of the next, in order to see if he can gain time by spending a few minutes upon it. In the interest of accuracy, however, the student must be careful not to have too many things in hand at once.

CHAPTER II

GENERAL METHODS OF ANALYSIS

THERE are three or four general methods of analysis; that is, the quantity of a particular constituent in a substance may be determined in three or four general ways.

1. **FIRST GENERAL METHOD.**—The simplest method is where the constituent required is extracted in some manner from the substance and weighed. From a mixture of iron and sulphur, the latter can be extracted by solution in carbon bisulphide, after which the carbon bisulphide may be evaporated and the sulphur weighed. Evidently, if one gramme of mixture provides ·2697 gramme of sulphur, the latter is 26·97 per cent. of the whole. In some cases the amount is not usually given in percentages. The percentage of gold in an ore is such a small fraction that the quantity is usually expressed in terms of ounces per ton. This does not indicate that a ton of ore has been treated. Often, what is called an "assay ton" is used. The assay ton contains as many milligrammes as the ton contains ounces. From the assay ton the gold is extracted, usually by means of lead, which is then got rid of, and the gold is weighed. Every milligramme represents an ounce of gold per ton of ore. This mode of analysis is very simple in principle but very limited in operation, because few substances can be easily separated from others in a state of purity. In a modified form, the same principle will be used in one or two analyses in this book. When barium chloride, containing water of crystallisation, is heated, water is driven off, and though not collected, its weight may be determined by the loss sustained by the salt on heating.

2. **SECOND GENERAL METHOD.**—The barium in barium chloride cannot be determined by any process of this kind; the barium cannot be extracted from the salt in such a way as to be determined directly. Its determination illustrates the

second general method. In this method, a compound, whose composition is known, is formed of the required substance, and from its quantity the quantity of the required substance is obtained. Suppose, for instance, one wishes to know how much barium there is in a given mixture of barium chloride and sodium chloride. If the mixture is dissolved in water and sulphuric acid is added, all the barium will go to form an insoluble substance, barium sulphate, which can be easily separated from the liquid by filtration and can be weighed. As the result of exhaustive analytical work carried on by many chemists, it is known that barium sulphate contains 50·85 per cent. of barium, hence when the quantity of barium sulphate which can be formed from the mixture of salts is known, the quantity of barium can easily be calculated. If a gramme of the mixed salts were found to produce 0·2 gramme of barium sulphate, the quantity of barium would be 0·1177 gramme, or 11·77 per cent. of the whole. Since it is easy to separate solids from liquids, in which they are insoluble, a usual method in analysis is to form an insoluble compound of the required constituent. Sometimes there are several insoluble, or nearly insoluble, compounds, and there may be alternative methods for a determination. Barium carbonate is nearly insoluble, also barium chromate, but neither of these compounds is so readily dealt with as barium sulphate, and neither is so frequently employed. Barium carbonate is not quite so insoluble as barium sulphate, and, moreover, when heated, is more liable to undergo some change. In the qualitative separation from magnesium and the alkalies of the barium group, which includes calcium and strontium, ammonium carbonate is added, and not sulphuric acid, because the carbonates are sufficiently insoluble, whereas calcium sulphate is sparingly soluble. Besides this, the mixed carbonates are more easily treated for the further separation of the individual members of the group.

It will be seen that advance may be made in quantitative methods by the discovery of new insoluble compounds, which may be more readily dealt with than those already known. Advance may also be made in finding out the best conditions for carrying out the operations already in use. It is now known that barium sulphate is precipitated in purer form if

precipitated slowly from a dilute hot solution, and these conditions are usually most satisfactory for other similar precipitates, but for some operations the best conditions are still very much in doubt.

3. **THIRD GENERAL METHOD.**—In the third general method of analysis, neither the particular constituent nor any compound of it is separated and weighed, but the amount of some other substance that must be added to use up, counteract, or neutralise the required constituent is determined; and from that by calculation, the required determination is made. For instance, if it is required to determine how much alkali there is in a soda ash, all that is necessary is to find out how much acid of a definite strength must be added to neutralise a certain weight of ash. Methods of this kind usually come under the head of volumetric analysis, because the quantities are measured in volumes. In the case above cited, one determines the volume in cubic centimetres of acid solution of known concentration that must be added to a given weight of soda ash dissolved in water, in order to make the liquid neutral in its action on the proper indicator. Where the substance is weighed, as in the first two general methods, the term, gravimetric analysis, is used.

4. There is a modification of the third method, which might almost be entitled to a division by itself, in which a comparison, usually of colour, is made with some standard. For instance, in determining the carbon in steel, the test steel and some standard steel, in which the carbon content is known, are treated with nitric acid in exactly the same way, and the solutions diluted till the shade is the same in both. The relative volumes of the solutions give a basis for calculating the amount of carbon in a test steel.

Silver is one of the substances which may be determined by any of the three general methods. In what is called the fire assay for silver, the silver is extracted by means of lead, as in the case of gold, and after the lead is got rid of, the silver is weighed. Instead of extracting the silver and weighing the metal itself, all of the silver in the ore may be obtained in the form of chloride and weighed. It is not difficult to convert the chloride into metallic silver, the chlorine being got rid of;

but that is unnecessary, since the percentage of silver in silver chloride is well known, and a calculation can be made instead of going through the operation of separating the silver from the chlorine. The determination may also be made according to the third general method by obtaining the silver as a soluble salt, such as the nitrate, and adding a solution of sodium chloride of known strength till the silver is all converted into chloride, and when this point is reached, the volume of sodium chloride solution used furnishes all that is needed for determining the amount of silver.

CHAPTER III

GENERAL DIRECTIONS REGARDING WORK

1. **TIDINESS.**—For the purposes of both accuracy and speed, tidiness is very important.

The work table should be kept scrupulously clean, the bottles containing acid and ammonia, which are in constant use, should be washed off at the beginning of each laboratory period, since, on standing for even a few hours, they become coated with ammonium salts, formed from the fumes of the laboratory or from the contents of the bottles themselves. Round the stopper distilled water should be poured. The lip should not be wiped off with a towel on account of lint or other dirt. Bottles used only occasionally should be similarly washed before pouring out the reagent. No stopper of a bottle should be placed upon the table or held within the fingers in such a way that the part entering the neck of the bottle will be touched. Before a cork is removed from a bottle containing a solid, the dust must be carefully wiped from the edge with a very clean cloth or filter paper, and, of course, the cork must not be laid with its underside upon the table or any place where it could get the smallest particle of dust. It is best to lay it upon its upper side.

At the end of the laboratory attendance the desk should be left perfectly tidy; no burettes, water baths, or other apparatus should be left upon it.

2. **REAGENTS.**—Each student is responsible for the purity of the reagents which he uses. A reagent which looks cloudy should never be used without filtering, no matter how many have been taking from the same bottle. Reagents should be tested from time to time for possible impurities that might be injurious, such as silica in ammonia, or chlorides and sulphates, when these are to be determined, or would in any way vitiate the results. It need hardly be said that reagents should never be borrowed from another laboratory. It is difficult enough to keep reagents pure in the quantitative laboratory,

where all of the students are supposed to work with special neatness and where the reagents are specially pure to start with. In other laboratories, the reagents may be made from a lower grade of chemicals at the outset, are probably not made of the same strength, and are not likely to be so carefully guarded from contamination.

3. **BALANCE.**—A student should always use the same balance with the same set of weights. The weights in one set may not agree perfectly with the weights in another set, since, unless with specially standardised weights, the makers guarantee only that the weights will be consistent among themselves, not that they will be of *exactly* the weight stamped upon them.

The balance should be kept perfectly clean. If the balance is found dirty, owing to the carelessness of some one weighing previously, and if the student is afraid that he will disarrange the balance by cleaning it, he should at once report to the instructor. It need hardly be said that the one who was responsible for spilling material in the balance should have reported it at the time. Not only is dirt in a balance very slovenly, but it may even have a corroding action and destroy the delicacy of the apparatus. A soft rag or cotton wool may be used for rubbing off the base of the balance, usually for the scale pans a camel's hair brush is best.

4. **RECORD BOOK.**—A carefully kept record book is of great importance. As the work is being done, notes should be written in a rough note-book sufficiently fully to enable the student to remember the details required for his record book, which should be so carefully written, that if consulted years after, it would give information as to the difficulties met and how they were overcome. It scarcely need be said that when the student writes his report a couple of weeks after doing the work, and has to look up the text-book, to see the method employed, his record is of little value. The record should show the instructor just what was actually done, so that he can correct errors ; a reproduction of what is given in the text-book is useless for this purpose. All figures of weights or volumes should be recorded, not merely the figures obtained by subtraction, otherwise any mistake made in subtraction cannot be detected. Not infrequently the student finds upon

handing an incorrect result to the instructor that some mistake has been made in his calculations, hence all the important calculations should be in such a form as to be easily checked. No records of permanent value should be made on loose pieces of paper, which may easily be lost.

5. **NUMBER OF DETERMINATIONS.**—Determinations are nearly always made in duplicate. The beginner will find it useful to make three determinations instead of two. The first, being for the purpose of giving familiarity with the processes involved, may be somewhat roughly done, and will indicate where special care is necessary in the subsequent determinations. If these two determinations do not agree within the limits of accuracy required, the student, unless he knows where his error occurred, should discuss the results obtained with the instructor before repeating the work, and should be able to give such an account of what he did that the instructor may be able to help him.

CHAPTER IV

COURSE OF ANALYSIS

THE principles of the first general method are so simple that it need not be discussed, and the third, or volumetric method, calls for no special remarks at this stage, but some general directions regarding the second method are in place. It involves the use of the balance, which will now be considered.

1. **THE BALANCE.**—It is not the intention to describe a balance which will easily be understood by the student on examination, but it should be noted that the balance must be level. Provision is made for this by two or more set screws in the supports. Balances have a long pointer, which by its motion across a scale when the balance is swinging, shows which side of the balance is the heavier. When there is no weight on the scale pans and the balance is perfectly adjusted, this pointer swings about the middle division. Perfect adjustment is, however, not necessary. Unless the deviation is too great, it is better to observe the amount of deviation and make the proper correction, just as a watch which loses a second a day is not kept constantly readjusted.

The swing of the pointer is sometimes read to the right and left of the middle, but if the divisions are all counted from the left side instead of from the middle, the calculation never involves the negative sign. There are usually ten divisions on each side of the middle, so that counting from the left, the middle is tenth. If the pointer swings four divisions to each side of the middle, the readings from the left will be, respectively, 6 and 14. With these readings and no friction, the pointer would be swinging exactly round the middle. It will be seen that these numbers added give 20; and in general, whenever the sum of the readings is 20, the swings are exactly about the middle or tenth division. So if the sum of the readings is 18, the swinging is about the ninth division, or one to the left of the middle. Similarly, if the sum is 23, the pointer

swings about the 11½ division. We may, if we like, say that the zero of the balance is 10 or 9, or 11½, but it is more convenient not to divide by 2, but to say that the zero is 20 or 18, or 23.

If there were no friction, two readings of the swings would be sufficient; but if there is friction, three readings are required for accuracy, and as will appear from the examples below, three readings are enough.

If the first swing is 16, and if, without friction, the second swing is 4, it is evident that with friction the pointer would swing not so far to the left, and would reach, let us say, 4·2. On the return swing the pointer would not go so far to the right as before, but would reach 15·6. As compared with the second swing, the first is too great and the third too small, so the average between the first and third should be taken. This is 15·8, which added to 4·2, gives 20.

Since beginners usually have difficulty with the reading and interpretation of the swings of the pointer, another example may be given. Suppose there are a series of readings, 14, 4, 13·7, 4·2 and 13·4. By adding the average of the first and third to the second, 17·85 is obtained; the average of the second and fourth added to the third gives 17·8, and the average of the third and fifth added to the fourth gives 17·75. The second place of decimals in this case has no significance; even a difference of one or two, in the first place of decimals, is ordinarily of no consequence, because the balance is not expected to be accurate within this limit. The ordinary analytical balances do not profess to read more accurately than to one or two tenths of a milligramme. The zero is in this case, approximately, 17·8, but if it is called 17·7 or 17·9, it would not make any appreciable difference in the weighing. Indeed, two successive determinations of the zero might readily differ even more.

In order to learn to how much weight one scale division is equivalent, the student should first find the zero of the balance without any weight, and then place the little wire, usually called the rider, on the first division of the beam. The rider usually weighs 1 centigramme, and as the first division is one-tenth way out on the beam, its effective weight in that position is 1 milligramme. Suppose the zero of the balance is

21, and when 1 milligramme is put on it changes to 16, it follows that there are five divisions of the scale for 1 milligramme, or half a division of the scale for one-tenth of a milligramme.

To illustrate what use may be made of the swings, let us suppose that in weighing a crucible, weights amounting to 10·17 grammes have been placed on the scale pan, and that the rider is on the sixth division. If the zero of the balance was 21, and if with these weights, the swings add to the same figure, the weight of the crucible is 10·1760 grammes, but if the swings add to 23·4, it is evident that the crucible is heavier than 10·1760 grammes, and the question is, how much heavier ? The difference between 21 and 23·4 is 2·4 divisions, and since five divisions correspond to a milligramme, 2·4 divisions correspond to ·5 milligramme, and the weight is 10·1765. On the other hand, if the swings had added to 19·7, the weight 10·1760 grammes is evidently too much, and the calculation shows that between two and three-tenths of a milligramme would need to be subtracted, the weight being 10·1757, or 10·1758 grammes, and these numbers are so close that it is a matter of indifference which is chosen.

When the balance is not in use, the beam is supported in such a way as to relieve the knife edges upon which the swinging parts vibrate when the weighing is being made. The beam is lifted from the supports by turning a handle in front of the balance. No chemical should ever be placed on the scale pan direct, but should be weighed in some containing vessel, or, in some cases, upon paper. Usually a salt is weighed in a weighing bottle.

2. **THE PROCESS OF WEIGHING.**—Let us follow the course of a weighing. First, the object to be weighed is placed on the left-hand scale pan, the handle which raises and lowers the beam is held in the left hand. Then upon the right-hand scale pan (of course, while the beam is resting on its supports), a weight should be placed which is almost certain to be too great. For instance, if the object is suspected to be between 40 and 45 grammes, the 50-gramme weight should be tried. This is because there might be a mistake in the estimate, and if the weight should chance to be over 50 grammes instead of

under, this would not be found out by using the small weight until they had all been put on the scale pan, and then they would need to be removed and the 50-gramme weight put on. The rule applies all through the weighing. Do not pass over any weight unless *certain* to be too large.

The left hand should not be removed from the handle until all the weights required have been put upon the pan. Beginners frequently put the weights on with their right hand, and then use the same hand for turning the handle, whereas if the handle is turned by the left hand immediately after the weight has been placed upon the pan, the right hand can remain in the balance case, ready at once to remove the weight if it is too large. Moreover, the handle should always be firmly held, else there is the chance of its being jerked by the sleeve or in some other way, and when the weights on the pan are unequal, a jerk will probably throw the beam off its bearings, making it necessary to remove all the weights and to readjust it. Some balances have a special contrivance for supporting the scale pans, but the student can easily make the appropriate modifications in procedure if using such a balance.

When a weight is too small, nothing is removed from the scale pan, but a new weight is added; when too large, the weight which has just been added is removed and the next weight put on. Until the sum of the weights on the right-hand pan is very near to the weight on the left, the handle will need to be turned only a slight distance, in order to find out whether too much or too little has been placed on the pan, and immediately this is done the handle should be turned back to bring the beam to rest before any weight is taken off or put on. Beginners often waste a great deal of time in this operation, and for this reason the instructions have been given minutely.

The weighing of an object whose weight turns out to be 39·6974 grammes would be much as follows: Put the 50-gramme weight on the scale pan; it would be too large, and must be exchanged for the 20-gramme weight, which is too small. Add a 10 gramme, still too small; add a second 10 gramme, too large; exchange 10 gramme for 5 gramme, too small; add 2 gramme, too small; add 1 gramme, too small; add another 1 gramme too small. It is now not worth while

to add the other 1-gramme weight, because that would add up to 40 grammes, which has already been found to be too much. The beginner may, however, feel more satisfied to do this and thus check his former observation. The fractional weights are now added: 0·5 gramme is too small; add 0·2 gramme, too large; exchange for 0·1 gramme, too small. Then add ·05, too small; add ·02, too small; add ·01, too small; add another ·01 gramme, too large. The weight is thus between 39·68 grammes and 39·69 grammes. The balance case is now closed and the rider used. (Unless the balance is closed, draughts may interfere with the weighing.) The rider is moved about till the swings indicate that the weight is within a milligramme of that required. Usually, two or three trials will be enough, and after a little practice, the proper position for the rider is often hit upon at the first attempt. In the assumed case, it would probably have been noticed that the balance started to swing more rapidly when the weight 39·68 grammes was upon the scale pan than when the weight was 39·69 grammes, hence the rider would naturally be placed towards the end of the beam. Let us assume that the zero of the balance has been found to be 21, that five divisions correspond to a milligramme, and that the rider is on the seventh division. The sum of the readings of the swings will now be approximately 23, showing that 0·4 milligramme must be added. If the rider had been placed on the eighth division the reading of the swings would be, approximately, 18, which would show that the weight on the beam was too great by 0·6 milligramme, which would, therefore, need to be subtracted. Either calculation would indicate that if the rider were placed at 7·4 there would be perfect balance, and the weight is, therefore, 39·6874 grammes.

Beginners often think that it is easier to move the rider till there is complete balance than count the swings and make the calculation; but calculation takes less time, and the less the time in weighing, the greater the accuracy, because there is always a likelihood that the weight will change, due to absorption from the air. If the student thinks that less time is required to move the rider than to make the calculation, it is because he does not understand the process, and he should ask help from the instructor.

The sensitiveness of the balance, that is, the number of divisions on the scale corresponding to a milligramme, remains pretty constant, and the student after determining it should keep it in his memory; the zero may vary readily, especially if a number of students use the same balance. A very slight mishap, or even an irregular change of temperature, may cause a variation in the zero, hence, unless two consecutive weighings are to be made and the difference between them taken, the zero must be determined. The zero of the balance should not be more than three or four divisions on either side of 20, and calculations of more than a milligramme should not be made by swings, because when swings have a wide amplitude they are not exact. The pointer should vibrate within five or six divisions from the middle. If the zero is not within the prescribed limit the instructor should be applied to, unless the method of adjustment has been learned.

3. **WEIGHTS.**—Each weight has its assigned place in the box, except where there are two weights of the same value, which are interchangeable. Care should be taken that the weights are put back into the proper place and in the proper position. The weight on the pan can be read by observing what places are vacant in the box, but a check should always be made by adding up the weights as they are removed from the balance and placed in the box. This check is specially necessary when several persons are using the same set of weights.

Of course, care must be taken of the weights as well as of the balance. The weights should never be lifted by the fingers, but by pincers. The box should always be kept closed when not in use, so that the weights may not become dusty or tarnished. Sometimes a small weight is lost. If it cannot be found, the loss should be at once reported. If a weight is missing when a student begins to weigh, he must not assume that it has been already reported, but should at once tell the instructor, unless he can himself find it. Great care should be taken not to lose weights and not to break little pieces from the small weights. They should be carefully examined from time to time, in order to see if they are all right.

4. **SPEED IN WEIGHING.**—The time required for a weighing is about five minutes ; if a student takes very much longer, he should find out how to increase his speed.

5. **WEIGHING MATERIAL FOR ANALYSIS.**—In beginning an analysis, the first step is usually to weigh the substance to be analysed and place it in a beaker (or porcelain dish). The process about to be described is a typical one, such as would be employed in the determining of chlorine or of barium in barium chloride, or of the sulphate radical in magnesium sulphate. The salt is weighed in a weighing bottle, of which it is well to know the approximate weight, in order to have some idea of the weight in the bottle. This is advisable, because the amount of salt taken for analysis should be about 0·3 or 0·4 gramme, and if it is known that the amount of salt weighs, approximately, 2 grammes, it is easier to judge how much to empty out than if there is doubt whether the amount is 2 or 10 grammes. The weighing bottle with the salt should never be enclosed by the hand or put in a place where it may become warm or moist. It should be held as lightly as possible between the thumb and one or two fingers. The heat of the hand might raise the temperature, so that the bottle would weigh a milligramme lighter than it should, because producing an upward current of air on the scale pan. Moisture on the hand might, of course, increase the weight considerably.

The weight of the bottle and salt is carefully determined to the fourth place of decimals. Then the weighing bottle is held over a beaker and the stopper withdrawn, and an amount of salt is shaken out by a gentle rolling motion of the bottle. The stopper is all this time held over the beaker, lest there should be any particles of salt on it, which might fall off. The bottle is then turned upright, tapped with the stopper to shake down any salt sticking to the sides, and the stopper is replaced. Not till then is either bottle or stopper removed from above the beaker. The bottle, with the remaining salt, is again weighed, and into another beaker is brought in the same way a second quantity of salt. Three weighings only are thus necessary for the two lots of salt, whereas, if the weighings were not all made at the same time, four weighings would be required. The weights should be put down in the note book

in three lines, so that the subtraction can easily be made. The form may be something like the following :—

Weight of bottle + salt . . .	12·4267	
		·3525
After taking out first quantity . .	12·0742	
		·3248
„ „ second „ . .	11·7494	

If three lots are to be taken for analysis there would be a fourth weighing. It is again urged that weighings such as these should not be entrusted to a loose piece of paper and that all the weights should be kept, not just the figures obtained by subtraction.

For the purpose of determining these weights it is unnecessary to find the zero of the balance. It may be assumed to be 20, because if it were 22, let us say, and not 20, the weights would all be correspondingly less, and in the case of a balance with five divisions for a milligramme the weights would be :—

12·4263	
	·3525
12·0738	
	·3248
11·7490	

The weights of the salt taken are, evidently, the same as before.

6. **BEAKERS.**—The beakers into which the weighings are made must, of course, be scrupulously clean. They should be thoroughly clean on the outside as well as on the inside, mainly because unless clean on the outside it is almost impossible to be sure that they are clean on the inside. After the visible dirt has been removed by the ordinary process of washing, the beaker should be washed inside and outside in the running tap water and then rinsed with distilled water. It may then be wiped on the outside with a clean towel, but not on the inside. There are few occasions on which a beaker or porcelain evaporating dish should be dried on the inside. It is much cleaner when simply rinsed with distilled water. It will be seen that the cleanliness of the chemical analyst must be considerably greater than that of the most tidy housewife.

It has been said that the most suitable weight of salt for analysis is usually 0·3 gramme or 0·4 gramme. This is a compromise. It might be thought that a larger quantity

would be better, because any error in weighing or any slight loss or gain in the process of analysis would make less percentage error. But, on the other hand, large precipitates are difficult to deal with ; they need large filter papers, they take a longer time for washing, there is more danger of loss in transferring to the crucible for ignition, and the ignition is not so readily completed. If a quantity much smaller than 0·3 gramme is taken, any errors in weighing or manipulation have too large a relative value, and it is usually inadvisable to go much below this amount. When one is analysing an ore, the amount to be taken depends very much on the probable percentage of the required metal, and may, in some cases, be as much as several grammes.

As the quantity of salt chosen for analysis is a compromise, so also is the quantity of water to be used and, therefore, the size of the beaker. The more dilute the solution from which the precipitation is made, the less likelihood, other things being equal, is there that any of the mother liquor will be enclosed with the precipitate. From this point of view, the more dilute the solution the better; but, on the other hand, no precipitate is perfectly insoluble, and a large volume of water involves the use of a large beaker, from which it is difficult to thoroughly clean out the precipitate. For what are ordinarily called insoluble precipitates, such as barium sulphate, silver chloride, calcium oxalate, 200 c.c. or 250 c.c. is a suitable volume for 0·3 or 0·4 gramme of salt. For holding this amount a beaker of about 450 c.c. should be used. The size of beaker should be about double the volume of the liquid to be contained. If the beaker is much smaller than this, there is danger of spattering when the liquid is stirred, and it is not very easy to pour out the liquid without some running down the side of the beaker. If the beaker is larger than double the volume of the liquid, there is an unduly large surface to be cleaned during filtration, and time is lost. The size of beaker should always be in proportion to the quantity of liquid that it is intended to contain.

7. **PRECIPITATION**.—If the precipitation is to be made in a hot liquid, the proper amount of boiling water should be added. This is better than adding cold water and heating to boiling in the beaker. It is quicker, because water may be heating

while the weighing is being made ; besides, during the heating of a beaker special care must be taken to avoid spurting. It is unsafe to heat to boiling, above a flame, a beaker with even a considerable quantity of liquid, without constant stirring with a stirring rod, since sudden boiling with bumping may occur and cause loss. Sometimes the student is tempted to leave the stirring rod in the beaker, on which a cover glass is placed, in order to make the boiling more uniform and less dangerous. The boiling is likely to be less vehement, but sometimes a sudden bumping occurs and the rod may make a hole in the beaker, which is, of course, fatal to the analysis.

Very frequently, in addition to the precipitating reagent, some other substance is added, for instance, nitric acid along with silver nitrate, in the precipitation of a chloride and hydrochloric acid or ammonium chloride with sulphuric acid to precipitate barium. These substances help to make the precipitate settle readily, and sometimes, but not always, prevent the carrying down of contaminating substances. The presence of acids, bases, or salts, is of most importance in the precipitation of amorphous precipitates. Some amorphous precipitates are partially soluble in pure water, and even after being precipitated may be dissolved when washed in the filter with pure water. The wash water must, in this case, have something added to it which will lessen the solubility, and which, at the same time, can be got rid of before the precipitate is weighed.[1]

The precipitating reagent should be added in dilute condition and slowly, and is better to be hot if the precipitation is being done in the heat. During the addition of the reagent, the flame should be removed from below the beaker, and the liquid stirred by a vigorous, but even motion of the stirring rod. The sudden formation of crystals, giving many points for the escape of vapour, might cause spurting, unless the flame were removed.

[1] What has here been called solution is probably not solution in the strict sense but the *colloidal* solution of *reversible* colloids. The effect of the presence of electrolytes on the solubility of colloids is a subject too advanced to be taken up here. Possibly precipitates settle more readily in solutions of salts because surface tension between the liquids and the solids is diminished. It is well known that very finely divided clay settles more readily in the salt water of the ocean than in the fresh water of the river flowing into it.

While all precipitates are, to some extent, soluble in water, they are less soluble when a slight excess of the precipitating reagent is added. The probable reason for this phenomenon is discussed in an appendix on "Electrolytic Dissociation." Usually, for the purpose of almost complete precipitation, very little excess of reagent is required. The greater the solubility of the precipitate the greater should be the excess. If a large quantity of excess is required, directions to that effect will be given when the particular case is treated. The tendency is to add too great excess rather than too little. This procedure is especially to be deprecated when a number of constituents are to be determined one after another. If reagents are added for each precipitation in too great excess, the solution becomes so saturated with salts towards the end that an inconveniently large quantity of water must be added to prevent them crystallising out.

The approximate quantity of reagent required may frequently be calculated. If one knows the salt that is being analysed and the concentration of the solution used as reagent, the calculation is easy. Concentrated acids and ammonia are ordinarily supplied in the quantitative laboratory; the other reagents are, for the most part, either saturated solutions, if the salts are not very soluble, or of 5 per cent. or 10 per cent. strength if soluble to a greater degree. It should be noted that salts containing water of crystallisation are usually weighed out in that condition; hence, if the calculation of how much barium chloride should be added to a given weight of magnesium sulphate is to be made, the equation to be used is not

$$MgSO_4 + BaCl_2 = BaSO_4 + MgCl_2,$$

but

$$MgSO_4, 7H_2O + BaCl_2, 2HO = BaSO_4 +, \text{ etc.}$$

From this equation it will be seen that the weight of barium chloride required is practically the same as that of the magnesium sulphate. Hence, if the barium chloride solution has a concentration of one part in ten, approximately 5 c.c. would be needed for 0·5 gramme of magnesium sulphate, and so 10 c.c. would be more than ample. The calculation should never lead the student to neglect testing, because he must make allowance for the possibility that the reagent has not the

strength supposed, and it may even happen that the salt given him to be analysed is not what he thinks it is.

In case an expensive reagent is used, there is still greater need for calculation. The equation

$$BaCl_2, 2H_2O + 2AgNO_3 = 2AgCl +, \text{ etc.},$$

shows that the weight of silver nitrate required to precipitate the chlorine from barium chloride is $\frac{340}{244}$ times the weight of the barium chloride, and if the weight of silver nitrate used is one and one-half times that of the barium chloride, there would be sufficient excess. If, then, the silver nitrate solution has a concentration of one in twenty, 15 c.c. would be required to precipitate the chlorine from half a gramme of barium chloride. Barium chloride contains less chlorine than almost any chloride likely to be given for analysis; therefore, if the composition of the chloride supplied is not known, it is safe to add the amount of silver nitrate required for barium chloride, and then to test whether enough has been used.

In the majority of cases, though there are exceptions, the precipitate should be allowed to stand for several hours, or even over night, before filtering, because some very fine crystals or particles are usually formed as the precipitation takes place. If the liquid is allowed to stand, the smallest crystals dissolve and the material is deposited on the larger crystals. It has been proved that the solubility of very fine particles is greater than that of larger particles, so that a solution may be unsaturated for the very fine particles, and saturated or supersaturated for the larger particles. Moreover, the surface tension between the solid and liquid is such as to tend to lessen the surface, and the lessening of the surface is brought about by the dissolving of the smaller particles and the growth of the larger. As very fine particles run through the filter, the purpose of allowing the precipitate to stand is obvious. The dissolving of the smaller particles and the growth of the larger ones takes place more rapidly if the liquid is kept warm ; thus, barium sulphate which has been kept for three or four hours at a temperature of 60° or 80° C. may be filtered as readily as if it had stood over night at the ordinary temperature. As soon as the precipitate has settled sufficiently, if possible, before

the beaker is set aside, a little more of the precipitating reagent should be added, in order to see whether enough has been used. When the precipitate is slow in settling, especially after vigorous stirring, it is often a sign that sufficient reagent has not been added. If any precipitate is produced on addition of the reagent, more reagent must be added, with stirring, and the test again applied. Before the filtration it is well to test again. Naturally, the stirring rod remains in the beaker all the time, and the cover glass is put on when the beaker is set aside. It may be taken, as a rule, that anything quantitative must be protected from outside contamination by being covered as far as possible.

8. **FILTRATION.** (*a*) **Preparation of Liquid to be Filtered.**—Unless the precipitate is appreciably soluble in hot water, the filtration should be done in the heat, because a solution, when hot, runs through the filter much more rapidly than when cold. Boiling water has only one-sixth the viscosity of water at zero, in other words, would take only one-sixth of the time to run through the filter, other things, of course, being equal. Hence, while preparation for filtering is being made, the beaker should be heating. This is best done in a steam or water bath, the beaker being set in the bath, so that the liquid will be surrounded by steam. In the case of using a water bath, only a little water should be used, so that it may boil rapidly. It should not take more than five minutes for the contents of the beaker to become hot enough, that is, as hot as can be held in the hand during filtration. Sometimes it may be convenient to place the beaker on a steam plate or other hot plate, instead of in the bath. Heating in this way takes longer. If the filtration is to take place within a few hours after precipitation, it is often advisable to allow the beaker to stand all the time on the steam plate. The essential thing about the heating is that the precipitate should not be stirred up, as would be the case if the beaker were heated over a wire gauze by a Bunsen burner.

(*b*) **The Filters.**—Filters for quantitative work can now be obtained practically ashless. The filter used should, in general, be small. For most purposes 5½ cm. diameter, a standard size of Schleicher and Schull, is suitable. The size of filter is

usually determined by the bulk of the precipitate, not by the quantity of liquid to be filtered. The liquid will run through a small filter nearly as rapidly as through a large one, and a small filter is more easily washed. The filter should be large enough to be not more than one-third full when all of the precipitate has been brought into it. The size of funnel depends upon the size of filter. The filter should not come within quarter of an inch of the top of the funnel, and probably, even a slightly wider margin is better. On no account should a filter be used which is larger than the funnel, as it is then impossible to wash it.

(*c*) **Fitting of the Filter.**—The fitting of the filter is of the utmost importance. Funnels can now be easily obtained with the correct angle, 60 degrees, so that the filter need only be folded in four quadrants, but if by chance the funnel has too wide or too narrow an angle, the folding of the filter can be adapted to it. The filter should be placed in the funnel without being moistened, until it is seen that it will fit. Then it should be wet, and the paper pressed against the funnel with the finger or thumb, so that no air bubbles are left between the paper and the glass. This fitting should be begun where there is the single thickness of paper next to the inside fold, and gradually worked round. The place requiring greatest care is where the fold is next the glass, because there is danger of a passage being left for air or for the precipitate to be carried down. The inside fold of the filter not being pressed down till the last, gives an opportunity for the filter to adapt itself completely to the funnel.[1]

The stem of the funnel should be quite full of water and remain full, even when all the water has run out from the filter. This is very important, because, if bubbles of air get in, they

[1] The action of a filter is sometimes more rapid if the filter be fitted as follows: With a funnel of 60 degrees the paper is folded with an angle slightly greater than 90 degrees, and the upper corner of the fold, which will be nearest the glass, is cut off to prevent the formation of an air channel. The upper portion of the paper should fit the funnel closely, and the tip should hang over the centre of the stem. Since the upper part of the filter fits closely there will be a space between the funnel and the paper at the lower part, which may allow more easy passage of the filtrate. There is little advantage with small filters; with large filters the speed is, in most cases, appreciably increased. The method is not recommended for beginners.

make the filtering much slower. Moreover, if the stem does not remain perfectly full, it is an indication that the filter does not fit properly, and during the filtration some of the precipitate may run through. A filter that does not fit may sometimes be made to do so by filling the funnel completely with water, drawing up the filter for an instant with the finger, till the flow of water drives out the air, and then allowing the filter to settle back into place immediately. With some funnels, it is almost impossible to make the stem remain full of water. Such funnels should be discarded. Often, by making one or two constrictions in the stem, by drawing out slightly in a flame, the stem may be made capable of retaining water. Funnels with a long stem are often recommended, since they give the suction of a greater column of water, but frequently, the friction more than counterbalances this advantage, and a funnel with a very short stem may chance to give excellent results. In the process of fitting the filter so far described, it is most convenient to use tap water, but the filter should now be washed out with distilled water, preferably hot. Pure, hot water should run through the filter at the rate of five or six drops a second, or even in a continuous stream, otherwise the filtering will take longer than it should.

If the filtrate is wanted, care must be taken that none of it shall be lost, and it is therefore best to place the receiving beaker so that the stem of the funnel will touch it in such a way that the liquid will run down its side, instead of splashing. Probably this precaution increases the speed as well.

(*d*) **Process of Filtration.**—The filter being properly prepared and the beaker hot, filtration is begun. The stirring rod is withdrawn as gently as possible, so that the precipitate will not be disturbed, and is placed against the lip of the beaker and the supernatant liquid poured off through the filter. In case the beaker has no lip, or when one is pouring from a flask, it is well to rub a very slight amount of vaseline on the outside of the rim where the liquid is poured out, so that it will not run down the outside.

It is best not to allow the liquid to quite fill the filter, though, should it chance to reach a little above the paper, no great harm should result. It is better that the liquid should overflow the filter than that it should not be run in rapidly enough to

keep the filter nearly full. It is important that the liquid should be run in continuously, as fast as it runs out, else the small amount of precipitate carried with it is likely to clog the pores of the filter and make the rest of the filtration slower. It is evident that if the filtration is going at all as it should, there is no time to remove the beaker from the funnel. One should not set down the beaker because the arm has become tired, unless there is danger that some of the substance will be lost, due to shaking of the hand. One should be careful to hold the arm in an easy position from the start, so that it will not become readily cramped. The student should aim at filtering 200 c.c. of the clear liquid in from three to five minutes, ten minutes is a long time, though if the precautions insisted upon are not taken, this part of the filtration may occupy half an hour or more.

As much of the precipitate as possible should be left in the beaker. When the liquid has run through, the filtrate should be examined, to see whether it is quite free from precipitate. This is best done by stirring with an even motion in one direction, in order to make an eddy which will gather the precipitate, if there is any, so that it will be easily seen against a proper background, for example, black, if the precipitate is white. Of course, if there is any precipitate in the liquid, it will need to be filtered again ; if the amount is small and it has settled well to the bottom of the beaker, as is likely to happen, with a heavy precipitate like silver chloride or barium sulphate, possibly a large portion of the supernatant liquid can be poured off without loss of precipitate, and only the remaining small quantity of liquid need be run through the filter. If this plan is adopted, the liquid should be poured into a clean beaker and carefully examined, to see that none of the precipitate has been carried away. Beginners are apt to suppose that unless the filtrate is to be used for a further determination, the receiving beaker need not be clean, but that this is a mistake is evident.

If the filtrate is quite clear and is not wanted, it should be thrown away before the washing of the precipitate is begun. If it is wanted, another beaker should be used to receive the washings, because a precipitate sometimes runs through the filter when it is being washed, and it is well to have as little liquid as possible to refilter.

(*e*) **Washing of the Precipitate.**—The problem now is to get all of the precipitate removed to the filter and to have it freed from the adhering liquid. For this purpose it is best to first wash several times by decantation. This means that a little water, say, 20 c.c., is poured upon the precipitate in the beaker (a drop or two of some reagent, which varies according to circumstances, is frequently added), the precipitate stirred, then allowed to settle for a minute, and the water poured off through the filter. After this process has been repeated two or three times, the precipitate is brought upon the filter. For this purpose a very little water, less than enough to fill the filter, is squirted into the beaker; the precipitate is stirred and poured at once into the filter. The precipitate is scraped down as well as possible with the stirring rod, getting out the last drop of the liquid, since the last drops carry with them a large portion of the precipitate; and the more that can be got out each time the better. After as much as possible has been removed by the stirring rod, there will probably still be a little precipitate sticking to the beaker. The best general method for removing it is to rub with a stiff feather specially prepared.[1] With the feather the stirring rod should be thoroughly cleaned, and the sides of the beaker rubbed down and squirted with water, which is then poured down the feather into the filter; after this has been done, till the beaker appears perfectly clean, it should be washed out a couple of times to make doubly sure.

Instead of a feather, a piece of rubber tubing on the end of a stirring rod may be used. In some cases, a small piece of filter paper may be rubbed round the beaker with the stirring rod, and the precipitate so loosened, squirted out along with the piece of paper into the filter. This method is not always allowable, and cannot be used unless the precipitate may be burned wet. Another method is to dissolve the precipitate by a suitable reagent and then reprecipitate it in a suitable

[1] This is done by cutting off the tip of the quill, and, leaving an inch or so of the feathery part at this end, stripping the rest of the quill. The feathery part that has been left is now clipped within a quarter of an inch or so on each side of the quill. The feather thus cut should be soaked for a few minutes in a test tube full of hot very dilute ammonia solution, then washed with water, then soaked in hot, very dilute hydrochloric acid, and, finally, well washed with distilled water.

manner. This mode is open to the objection that the re-precipitation may not be complete. Whatever method may be used for the final cleaning of the beaker, it should not be employed until all of the precipitate that can possibly be removed by the stirring rod has been got out, so that if there is any loss, it will be known to be only a fraction of the minimum.[1]

When the precipitate has been all removed to the filter it must be still further washed. Beginners are liable to think that only the visible precipitate in the filter need be washed, and they hesitate to fill the filter with water, lest they should wash some of the precipitate through it. But it is essential that the filter paper be completely washed out, because the paper absorbs solid from the solution and needs to be well washed to get rid of it. The quickest way to wash out a filter is to fill it quite to the top with water, either pure or, if necessary, containing some of the reagent prescribed for washing, then to allow the water to run out completely and to repeat the operation till the washings contain nothing that should be removed. If there is any precipitate in the funnel above the filter, it must also be washed. Care must be taken that the precipitate in being washed is not splashed out of the funnel. For that purpose, if a stream from the wash bottle is used, it must be steady, and should be directed first to the bottom of the filter and gradually brought towards the top. The nozzle of the wash bottle is usually attached to the delivery tube by a short piece of rubber tubing. The best way to get a steady stream for washing the precipitate is to start the stream running (into the sink or elsewhere), and then clamp the rubber tubing between finger and thumb and blow gently into the wash bottle before directing the nozzle into the funnel. While blowing, loosen the hold on the rubber tubing, and thus a stream of water will flow without the spurting caused by air. Before the blowing is stopped, and before the nozzle is withdrawn from the funnel, the rubber tubing should be again clamped, or the inrush of air may suck back some of the precipitate.

[1] It is sometimes possible to wash a precipitate out of a beaker by tilting it up and directing a stream of water from a wash bottle against the sides and bottom of the beaker behind the precipitate, and by this means flushing the precipitate into the filter. This method is not recommended until the student has gained some experience.

The precipitate must be washed much more frequently than one would naturally think necessary, because it retains or, as it is called, absorbs material from the solution. This is specially true of gelatinous precipitates, some of which cannot be fully washed out at all. In quantitative analysis, care must be taken to avoid precipitates of this kind, or to provide that the substance absorbed can be got rid of at a later stage, as, for instance, that it will be volatilised when the precipitate is ignited. In order to test whether the precipitate is washed as completely as possible, two or three cubic centimetres of the washings should be collected in a test tube and tested with some delicate reagent, as, for instance, silver nitrate for a chloride. If there is no precipitate, the washing is probably complete, but it is usually well to wash once or twice more to ensure greater security. As, however, no precipitate is perfectly insoluble, the test should be made before the washing has been often repeated. Frequently, by the time the precipitate has been completely removed from the beaker, all of the soluble impurities have been washed out.

If the filtration has proceeded satisfactorily, the stem of the funnel should still be filled with water. This should be removed best by inserting a capillary tube, which allows the liquid to run out while air passes up. The funnel may then be covered with a qualitative filter paper, in which a few holes are afterwards made with the point of a pencil, to allow of escape of steam, and the funnel placed in a hot water jacketed air bath. In this way the filter and precipitate are dried. The funnel should not be left longer than necessary in the air bath. When too many are in the bath at once, some are likely to be upset.

9. **IGNITION OF PRECIPITATE.**—When the precipitate is dried it should be ignited. In the simplest and most common case this operation is carried out as follows: The crucible, which has previously been cleaned, heated to redness, cooled in a desiccator, and weighed, is placed upon a piece of glazed paper eight or ten inches square lying on the table. The funnel containing the filter is held over the glazed paper, the filter carefully removed and the funnel laid upon the paper. The precipitate is removed from the filter to the crucible as far as can be done by a gentle rubbing together of the sides of the

filter, or perhaps, even by the use of a metal spatula. If any of the precipitate should chance to be spilled upon the glazed paper, the crucible should be placed upon another piece of glazed paper and the precipitate carefully removed to it. The filter is then carefully laid upon the glazed paper and another piece of filter paper, best half of a filter, the same size as the former, is moistened with a drop of water, and used to wipe the funnel clean. If there is any of the precipitate on the fingers or on the spatula, it should be wiped off on the same piece of paper. One half only of the filter which was in the funnel has precipitate upon it, and the filter is now folded along the diameter, so that this precipitate may be at one end of the half circle thus formed. The other piece of filter paper is fitted to this filter, and these are now folded with two creases parallel to the straight side, the diameter of the filter. It will be evident that if the filter paper were 6 cm. in diameter, the strip containing nine thicknesses of paper would be 6 cm. long and 1 cm. broad. The precipitate would be at one end of this strip. The strip should now be rolled as tightly as possible, beginning at the end containing the precipitate, so that it will be in the inside, and thus protected by many thicknesses of paper, and a platinum wire should be wound tightly round the roll in a spiral form, the windings not crossing, for they will afterwards need to be pulled apart. A good size of wire is ·016 mm. diameter and 20 or 25 cm. length. This length of wire will be sufficient to allow the free end to be fixed in a burner plate in such a way that the roll of paper may be over the crucible, which is now placed on the plate. The outer flame of the burner should be applied to the filter until it catches fire, and then removed and the hands placed round the burning paper to form a kind of chimney, which will make an upward draught. In all cases it is well—in some cases essential—to have the filter burn at as low a temperature as possible, hence, so long as the paper is burning at all, even smouldering, the flame of the Bunsen is not to be applied to it. When the burning has ceased altogether, there will still be a little unburned carbon, and the Bunsen flame should be flashed for a moment upon any places where such is seen, until it has disappeared. The ash should then be dropped into the crucible ; possibly the spiral of wire will need to be pulled apart,

and care must be taken that all of the ash falls into the crucible. The wire should be uncoiled carefully, so that there will be no kinks in it. Platinum wire is very pliable when hot, so if held in the flame it can be freed from uneven bends.

The crucible should now be placed in a triangle and heated, then removed to the desiccator, cooled and weighed; then heated once more, cooled and weighed; and this process should be repeated till the weight is constant. At what temperature the precipitate should be heated, how long, whether with crucible open or closed, depends upon the character of the precipitate, and directions will be given in each case, unless the full temperature of the Bunsen is suitable.

In some cases, the main precipitate should be kept till the filter has been disposed of, and only then brought into the crucible. In such cases, it may most suitably be put upon glazed paper and covered with a watch glass or funnel. These cases will be described as they occur.

Another method of igniting a filter is to burn it wet. This is applicable only in certain cases, usually those in which a platinum crucible is employed. They are the cases in which the presence of carbon will not reduce the precipitate to some undesirable compound. When the precipitate is burned wet, the filter is not rolled up as before, but just folded together a little and placed so that the apex of the filter is towards the mouth of the crucible in such a manner that the precipitate will be best protected from loss. The funnel, of course, must be wiped out and the paper used may best be placed upon the other which is in the crucible. Since the precipitate is wet, it is evident that the heating must be slow, or the steam produced would carry away some of the material. Some chemists recommend placing the crucible upright, high above the flame, and covered so that the filter may be dried and then charred, after which the crucible is lowered to the flame and the air admitted. Perhaps a better way is to lay the crucible on its side in the triangle, to lean the crucible lid against it and to apply a small flame to the outer part of the lid, which conducts the heat sufficiently to dry the paper, which afterwards begins to smoulder, or may even take fire. If the paper begins to burn, the flame should be removed, so that the burning will proceed very quietly. If in the flame there are little sparkles

which escape from the crucible, there is evidence of loss, because the sparkles are due to fine particles of the precipitate. The occurrence of the sparkles shows that the burning is too vigorous. After the filter has been burned, the crucible should be more strongly heated and the precipitate thus ignited.

As stated above, the precipitate must be reheated till the weight becomes constant. The crucible, when exposed to the air is liable to absorb a very little moisture, hence, the second time the crucible with the precipitate is weighed, the weights should be put upon the pan before the crucible is removed from the desiccator, and the second weighing, on this account, may be half a milligramme less than the first, but if the weight has diminished by more than a milligramme, the crucible, with precipitate, should be heated once more and again weighed after cooling, and the operation repeated till two successive weighings differ by not more than half a milligramme. Usually, one or two reheatings only will be necessary. The crucible should be weighed with the cover on, so that the precipitate will be as little exposed to the air as possible.

All of the weighings should be recorded in the book handed in to the instructor, so that it may be evident to him that the weight was constant. The weighings should be plainly shown in some way like the following, so that the figures can be seen at a glance.

Weight of crucible	.	.	10·4765
,,	+ ppt.	.	10·7259
,,	after heating again	.	10·7240
,,	,,	.	10·7235
,,	,,	.	10·7234

While a difference of a milligramme would be allowable between the first and second weighing, and further heating would be considered unnecessary, half a milligramme only would be allowed between two successive weighings after that, because, in these cases the weighings take, approximately, the same time, for the weight is known very nearly, and there is only the readjustment of the rider, if, indeed, that is necessary. If the two successive weighings differ by only half a milligramme, the probability is that the last one is practically correct.

10. **CALCULATION OF RESULTS.**—The precipitate having been weighed, it remains to calculate the percentage of the required constituent in the salt given for analysis. Suppose the precipitate is barium sulphate obtained from a barium salt, the amount of barium is evidently $\frac{137}{233}$ of the whole, as can be calculated from the formula $BaSO_4$. This quantity of barium was in the original salt, so that if divided by the weight of the original salt the fraction will give the percentage. On the other hand, if the original salt were a sulphate, the quantity of sulphur trioxide would be $\frac{80}{233}$ of the whole, and so the percentage in the original salt could be obtained. The fractions $\frac{137}{233}$ and $\frac{80}{233}$ are got by using the approximate atomic weights; in the Appendix there is a table giving the factors calculated from the more exact atomic weights, which show the ratio of the constituent desired to the substance weighed. The factor for the barium in barium sulphate is ·58851, found under the heading barium, and the factor for the sulphur trioxide in the same precipitate is found under sulphur to be ·34300. The logarithms of the factors are given in the same table.

If from ·4426 gramme of salt containing barium ·3769 gramme of barium sulphate is obtained, the actual amount of barium is

$$\cdot 3769 \times \cdot 58851,$$

and the fraction of the original salt is

$$\frac{\cdot 3769 \times \cdot 58851}{\cdot 4426}.$$

Inspection shows that this fraction is less than ·58851, and is not far from ·5 or 50 per cent. Exact calculation is easily made by logarithms, and since the characteristics of logarithms are needed only to give the position of the decimal point, they may be omitted. The calculation then is

Logarithm 3769	57623
Logarithm of factor	76975
·2218.	34598
Logarithm 4426	64601
50·11 per cent.	69997

The percentage of barium in the original salt is 50·11. Crystallised barium chloride $BaCl_2$, $2H_2O$ contains 56·15 per cent. of barium, hence, with the figures assumed, the salt analysed could not have been pure barium chloride, or else a very grave error was made in the determination. The number ·2218 given in small figures is the amount of barium in the barium sulphate obtained, and is the antilogarithm of 34598. Usually, the percentage only is required, and this number would not be looked up. The calculation of results can readily be made, and should be put down in the record book shown to the instructor, in such a style as to be easily checked.

Another calculation may be given. Suppose that ·3164 gramme of barium sulphate is obtained from ·3341 of salt containing sulphate and the sulphur trioxide is required. It is easily seen that it would be worked out as follows :—

Logarithm 3164	50024
Logarithm of factor	53530
	03554
Logarithm 3341	52388
32·48 per cent.	51166

As the amount of sulphur trioxide in crystallised magnesium sulphate, $MgSO_4$, $7H_2O$, is 32·52 per cent., the above result would correspond very well with it. Other calculations can be made in the same manner.

11. **CARE OF PLATINUM.**—The care of platinum, especially of crucibles, is very important. Since a crucible is subject to intense heat, it is necessary to make sure that it will not lose weight under the treatment. Hence, the crucible when received by the student should be tested. It should be thoroughly cleaned and then rubbed inside and out with fine sea sand which is rounded, not angular, or with Sapolio or something of the same nature. Then, after being rinsed finally with distilled water, it should be heated for a few minutes. Great care should be taken not to heat in the inner cone of the Bunsen, but in the outer oxidising cone. The inner cone contains unburned hydrocarbons, which act on the platinum, forming a carbide, and when this carbide is afterwards decomposed, the platinum is left flaky and brittle. While it is bad to

allow the inner blue cone of the flame to play upon the crucible, it is still worse to allow a luminous tip to touch it.

After the crucible has been heated for a few minutes, it should be cooled in the desiccator and weighed, then subjected to the flame of the Bunsen for half an hour. The lid should be placed upon the crucible and the whole should be maintained at a bright, red heat. If the weight now differs by more than half a milligramme from what it was before, the crucible should be again heated for half an hour in the Bunsen and, perhaps, for a few minutes in the blast. If the weight is not yet constant, the crucible should be rubbed once more with sand and the operation repeated. If the weight still does not become constant, the fact should be reported to the instructor. An old crucible is not likely to give trouble; with a new one, it is specially necessary to be careful in testing. Beginners hesitate to rub a new crucible with sand, but a new crucible most needs such treatment. Sometimes a new crucible develops blisters on heating, if so, it should be returned to the instructor. The main reason for rubbing with sand is that platinum tends to assume a crystalline structure, which rubbing prevents. Even if a crucible seems bright and clean, it should be rubbed with sand after the ignition of five or six precipitates.

To clean a dirty crucible, first try strong, hot hydrochloric acid; if that fails, wash out the hydrochloric acid and use nitric. If that should not serve the purpose, try in turn, fusion with acid potassium sulphate or sodium carbonate, or borax. The preparation of the crucible should be made to fit in with the spare minutes of some other operation, that it may be ready as soon as needed. The heating requires no attention, and can be going on while a precipitation or filtration is being made.

Substances containing an easily reducible metal should never be heated in a platinum crucible. These metals are usually those that occur in nature, as sulphides, or in the metallic state; lead, silver, arsenic, and so forth. The metals are liable to alloy with the platinum and destroy it. Fused caustic potash or soda also injures platinum, likewise nitrates and nitrites and sulphur.

Crucibles, whether platinum or porcelain, should be weighed with the cover on, and it is evident that the cover must have been heated.

CHAPTER V

BARIUM CHLORIDE

THE analysis of barium chloride involves the determination of chlorine, barium and water. The operations are nearly the same for other chlorides, such as potassium or sodium chloride, and for other barium salts, such as the nitrate.

1. **CHLORINE.** (TIME, SIX HOURS.)—The chloride which is most easily precipitated and weighed is silver chloride, and as silver nitrate is the most common soluble salt of silver, chlorine is determined gravimetrically by adding silver nitrate to the chloride. Silver chloride is darkened by the light, hence, as far as possible, the precipitate should be shielded, especially fron direct sunlight.

The process is as follows :—

(*a*) **Precipitation.**—Weigh out as described in the general directions, into 450 c.c. beakers, two lots of salt of about 0·3 gramme to 0·4 gramme. Add to one lot about 200 c.c. of cold water, and then about 5 c.c. more than the calculated amount of silver nitrate solution, to which about ½ c.c. of nitric acid is added.[1]

The reason that the nitric acid is added to the silver nitrate rather than to the chloride solution is, that if added to the chloride, chlorine might be set free and thus lost. It is well known that aqua regia, which is a mixture of strong hydrochloric and nitric acids, gives off chlorine, and though in the very dilute solution the danger might not be great, it is well to avoid it. When the chlorine is precipitated as silver chloride, the very dilute nitric acid will not act on it. The silver solution should be added slowly and with vigorous stirring, in order to coagulate the precipitate as much as possible. After the precipitate has settled sufficiently, add a little more silver nitrate solution. If more precipitate forms, add 5 c.c. or 10 c.c.

[1] The reason for adding nitric acid is discussed on p. 21.

more silver nitrate, stir vigorously and test as before. Usually, if the precipitate does not settle within a few minutes, it is pretty good evidence that the precipitation is not complete and that more silver nitrate must be added. When enough silver nitrate has been added, place the beaker in a steam or water bath and heat to about 70° C., with frequent stirring. If enough silver nitrate has been added, the precipitate will almost certainly settle, so as to leave the liquid nearly clear. Again test for complete precipitation, by adding a few drops more of silver nitrate and, if enough has been added, set the beaker aside over night so that the precipitate may be thoroughly settled. Of course, the stirring rod should be left in the beaker, over which a cover glass should be placed, and which should not be exposed to fumes of hydrochloric acid.

The second lot of chloride is then treated in the same manner as the first; or it is possible that the precipitation of the two lots can be carried on concurrently, or nearly so.

(*b*) **Filtration.**—The filtration should be carried out as described in the general directions, the beaker being heated in a water or steam bath. When the clear liquid has run through the filter, it should be examined to see if any precipitate has run through, and if not, the filtrate should be poured into the silver residue bottle and the washing begun. It may be advisable, in order to make assurance doubly sure, to add a drop or two of silver nitrate to the filtrate before emptying it. There should, of course, be no cloudiness produced, since all of the chloride should have been already precipitated. When washing by decantation and removing the precipitate from the beaker, it is well to add a drop or two of nitric acid each time with the water. If there is a film of silver chloride which is difficult to remove from the beaker, it may be dissolved off by a little dilute ammonia and reprecipitated by nitric acid. Use the smallest amount of ammonia necessary, just a drop or two of strong solution added to a little water, and then add enough nitric acid to produce a cloudiness. A drop of silver nitrate will help the precipitation. Then warm and stir, to coagulate the precipitate as much as possible. This precipitate will even then be more finely divided than that on the filter, but the filter will probably be

by this time sufficiently clogged to prevent it running through. This method of removing the precipitate, however, should be employed only after all of the loose precipitate has been washed out. Wash the beaker out two or three times after the reprecipitation and then wash the precipitate on the filter, finally with pure water, till nitric acid and silver nitrate are washed out. It is evident that the silver nitrate must be washed out, else it would increase the weight of the precipitate on burning. Nitric acid would make the filter brittle when dried. Two or three washings will remove the acid; to make sure that all of the silver nitrate has been washed out, collect about 3 c.c. of washings in a test tube as they run through the funnel and add a drop of hydrochloric acid. Washing should be continued until there is no cloudiness produced by this test. Only a drop of acid should be added, since excess of hydrochloric acid might dissolve silver chloride. The precaution insisted upon in the general directions, that the top of the filter paper must be washed, is again urged; after filtration, remove the water from the stem of the funnel, and after covering the funnel as described, set it aside in the drying cupboard.

(*c*) **Ignition.**—A platinum crucible must not be used for ignition of silver chloride, because it would be attacked; a porcelain crucible is used instead. Remove the precipitate as far as possible from the filter, without carrying with it shreds of paper, place it upon glazed paper and cover. Burn the filter in a platinum wire, as described in the general directions, but with very special care, since the hydrogen of the paper tends to remove chlorine from the silver chloride, and give metallic silver, which, if heated too strongly, would melt and alloy with the platinum wire. By taking care that the precipitate shall be protected by the folds of paper outside, and by using as low a temperature as possible for burning the paper, the danger may be avoided.

The silver produced by reduction of the chloride must be changed again to chloride, and since silver is little, if at all, acted on by hydrochloric acid, a somewhat indirect method is used. Allow the ash to fall into the crucible; add a drop of nitric acid and heat the crucible gently, in order to dissolve the silver, and then add a drop of hydrochloric acid and heat to dryness. After this operation has been completed, bring the

main body of the precipitate from the glazed paper into the crucible. This is best done by placing the crucible on another piece of glazed paper eight or nine inches square, and carefully pouring the precipitate into the crucible. Possibly, the last particles may need to be brushed down with a spatula or camel's hair brush, which should be used only if necessary. In any case, care must be taken, and especially if a brush is used, lest the precipitate should stick and not be transferred to the crucible. Of course, the brush must be freed from dust before it is used. If, by chance, any particles of the precipitate should have fallen outside the crucible on the second glazed paper, they must be brought into the crucible.

If the precipitate is dark, it is possible that a little chlorine has been lost, since the darkening is thought to be due to the formation of sub-chloride, and in this case, add a drop of nitric acid and a drop of hydrochloric, and heat the crucible very cautiously to drive off the acids without spurting. Then heat the precipitate gently, to below a red heat, for a minute or two, just till the precipitate begins to fuse at the edges. If too strongly heated, a little silver chloride may volatilise, but the precipitate must be heated strongly enough to drive off all the moisture. It is well to hold the lid in the tongs above the crucible, so that the process can be seen, otherwise the precipitate is almost certain to be heated too strongly. After cooling in a desiccator and weighing, heat again as before, and the weight will probably be constant. If not, the operation must be repeated.

The best way to loosen the silver chloride from the crucible is by dilute sulphuric acid and a little zinc. This changes the silver chloride in part to metallic silver. Ammonia may be used instead of zinc and sulphuric acid. The loosened mass should be put into the silver residue bottle.

It will be seen that the total determination needs, at least, part of three laboratory attendances. If possible, the two filtrations should be done at the same attendance, but *separately*. A filtration must be going very slowly, indeed, if it is possible to run two together. The two ignitions can be run concurrently, that is, while one is cooling, attention can be given to the other.

Six hours is a reasonable time for the determination, namely,

two for the weighing out and precipitation, two for the filtration and two for the ignition. As stated in the general directions, if the two results do not agree, the instructor should be consulted before another determination is made.

2. **WATER.**—Into a weighed platinum crucible put between half a gramme and a gramme of the salt; weigh the crucible and salt together and, with the cover on the crucible, heat gently, so that the decrepitation caused by uneven expansion of the crystals by heat may be as little as possible, and that if it does take place there will be no loss from the spurting. The temperature should be kept below dull red, except for a minute or two at the end. Cool and weigh, and repeat the heating to a constant weight. The two determinations of water can be made concurrently with the precipitation and filtration of barium.

Though potassium and sodium chloride have no water of crystallisation, they are liable to absorb a little moisture which could be determined in the way just described.

3. **BARIUM.** (TIME, SIX HOURS.)—As already stated, barium is usually determined in the form of sulphate.

(*a*) **Precipitation.**—Weigh out two lots of barium chloride of 0·3 gramme or 0·4 gramme each into 450 c.c. beakers. Add to one lot boiling water (which should have been heating while the weighings were being made) till the beaker is nearly half full, then add about ½ c.c. of hydrochloric acid (or about a gramme of solid ammonium chloride). Bring to boiling by heating over a wire gauze, constantly stirring with a glass rod, remove the flame and add to the liquid about twice the calculated amount of strong sulphuric acid diluted with thirty or forty times its volume of water. It is a common mistake to add far too much acid. Remember that sulphuric acid is nearly twice as heavy as water (specific gravity, 1·84). The sulphuric acid should, of course, be added to cold water, but it is well to heat the mixture before adding it to the boiling solution of barium chloride. As stated in the general directions, the reagent should be added slowly and with constant stirring, the flame having been removed from beneath the beaker. In this case, it may be a second or two before any precipitate appears. This is satisfactory, as the precipitate

is then less likely to enclose mother liquor. After the sulphuric acid has been poured in, heat the beaker for two or three minutes with constant stirring. It is best to heat to boiling, but if there is any danger of spurting, it is better to stop heating rather than to run the risk of loss. Barium sulphate is heavy and settles quickly and, as soon as the supernatant liquid is clear enough, a drop or two of dilute sulphuric acid should be added to make certain that the barium has been completely precipitated. The beaker may then be set aside over night, or if it is desirable to filter within a few hours, it may be possible to do so if the beaker is kept at a temperature of about 80°. The second lot is precipitated just like the first.

(*b*) **Filtration.**—Barium sulphate is one of the precipitates that are liable to run through the filter, so the filtration requires care. After the beaker and its contents have been heated in the water bath, the clear liquid should be filtered and examined, to see whether any precipitate has been carried through. If not, the filtrate may be thrown away, but if for any purpose you wish to keep it, use another beaker for the washings. Wash the precipitate by decantation, adding a few drops of hydrochloric acid to the water to facilitate the washing. Some of the precipitate will, doubtless, be carried into the filter, and usually it clogs the pores of the filter sufficiently to prevent the precipitate running through. After two or three washings by decantation, bring the precipitate into the filter, cleaning out the beaker, as described in the general directions. For the last particles, it is best to use a prepared feather, but if that is not convenient, a small piece of filter paper may be rubbed round the walls and bottom of the beaker by a glass rod, and brought with the rest of the precipitate into the filter. Of course, the beaker will need to be squirted out a number of times after having been wiped with the paper. Probably, by this time, the precipitate and filter will be nearly washed out, but they should be washed with hot water till there is no chloride to be detected, by addition of a drop of silver nitrate solution to about 3 c.c. of the washings.

If the filtrate that first passed through the filter was not clear, it will probably suffice to run it through the same filter again before beginning to wash the main precipitate; if it

still continues to run through, the best plan will be to wash the filter with the small quantity of precipitate upon it, and refilter the cloudy filtrate through a filter of closer texture (No. 595 Schleicher and Schull, the packages of which are wrapped with a blue band), and bring into it the main precipitate. In any case where it is feared that the precipitate will run through the ordinary filter, it may be well to use the special one, which filters more slowly. It is more satisfactory to filter once slowly than to have to refilter.

(*c*) **Ignition.**—The precipitate may be burned either wet or dry. If filter paper has been mixed with the precipitate, it will be better to burn it wet. No special precautions are required beyond those given in the general directions. The precipitate should finally be heated for twenty minutes at the highest temperature of the Bunsen, and reheated till the weight is constant. There is a possibility that some of the barium sulphate may change to sulphide, but if there is free access of air, this will probably change to sulphate again. Some chemists advocate treating the precipitate with a drop of sulphuric acid to ensure the change, and it would be well, after getting a constant weight by simple ignition, to add a drop of sulphuric and heat very gently till the acid is driven off, and then strongly for ten minutes, and to see if the weight increases. If it does, the precipitate should be heated again to constant weight.

If the precipitate is burned dry, there is less danger of the formation of barium sulphide. The precipitate is removed directly to the crucible, the filter burned in the platinum wire and the ash allowed to fall into the crucible. None of the special treatment required in the case of silver chloride is needed here.

The determination of chlorine, water and barium should take about fourteen hours. Possibly the free time in the ignition of barium sulphate might be used in weighing out and precipitating the salt of the next determination.

CHAPTER VI

MAGNESIUM SULPHATE

1. **MAGNESIUM.** (TIME, SIX HOURS.)—(*a*) **General Considerations.**—The determination of magnesium is important from several points of view. Magnesium is a common constituent of rocks, and is, therefore, frequently met with. Moreover, its determination necessitates manipulative care in various respects, which thus gives training to the student. In addition, the chemical reactions involved are very instructive. There is probably no quantitative determination which more fully illustrates the connection between analytical chemistry and general chemistry, since the determination of magnesium as phosphate is connected with the reactions of phosphates in general. Perhaps half the value of the determination is in the consideration of the chemical reactions concerned. The discussion of these is entered into somewhat fully in the Appendix to this chapter, which the student is advised to read before proceeding with the work ; the more strictly analytical treatment of the subject is given here.

Of the compounds of magnesium that can be used for determining the amount of the element in a magnesium salt, none is as insoluble as silver chloride or barium sulphate, and the determination of magnesium presents several difficulties. It can be best precipitated as magnesium ammonium phosphate, which is readily soluble in acid, slightly soluble in cold and more soluble in hot water, very slightly soluble in dilute ammonia. The method usually employed for producing this precipitate is to add sodium phosphate to a fairly concentrated solution of the magnesium salt containing ammonia. The reaction is represented as taking place in accordance with the following equation, in which the water of crystallisation of the different salts is omitted, as not affecting the principle :—

$$MgSO_4 + Na_2HPO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

The precipitated magnesium ammonium phosphate is not weighed in that form, but by heat it is converted into magnesium pyrophosphate, as represented by the equation

$$2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$

When ammonia is added to magnesium sulphate, magnesium hydroxide is formed as a white, gelatinous precipitate.

$$MgSO_4 + 2NH_4OH = Mg(OH)_2 + (NH_4)_2SO_4.$$

The hydroxide is not completely precipitated, and, therefore, cannot be used as a method of determining magnesium. The action is, indeed, reversible, and addition of considerable ammonium salt prevents precipitation of magnesium hydroxide by means of ammonium hydroxide. This fact is made use of in order to avoid contamination of the phosphate precipitate with magnesium hydroxide. Ammonium chloride is the most convenient salt to use or, what comes to the same thing, hydrochloric acid and ammonia may be added in succession.

(*b*) **Precipitation.**—Put about 0·4 gramme of magnesium sulphate into a 100 c.c. or 200 c.c. beaker (possibly it will be best to use a beaker of each size for the duplicates and to compare the results). Pour in cold water till the beaker is about one quarter full, add about 2 c.c. of strong hydrochloric acid and then ammonia, till the solution is alkaline, as can be detected by the smell. If magnesium hydroxide is precipitated, add more acid and more ammonia, until the required excess of the latter gives no precipitate. Then add slowly, with vigorous stirring, about twice the calculated volume of sodium phosphate solution, a saturated solution of which contains about 10 per cent. of Na_2HPO_4, $12H_2O$. In making the calculation of the quantity required, the water of crystallisation, both in this salt and in the magnesium sulphate, $MgSO_4$, $7H_2O$ must be taken into account.

Though the stirring should be vigorous, care should be taken not to touch the sides of the beaker, because crystals of the precipitate stick to the places touched and are hard to remove. Of ammonia of specific gravity 0·96, add a quantity which is about one-third the volume of the liquid now in the beaker. This strength of ammonia is, approximately, obtained by

diluting ordinary strong ammonia with its own volume of water. Let the precipitate settle over night.

(*c*) **Filtration.**—Filter in the cold, with the use of as little water as possible for washing. The precipitate, if properly produced and allowed to settle, should be coarsely crystalline and need not be washed by decantation so much as less markedly crystalline precipitates. Add a little ammonia to the water used for cleaning the beaker, and when no more precipitate can be got out by means of a glass rod, use a feather. If some precipitate persistently sticks to the beaker, dissolve it with a little hydrochloric acid and reprecipitate with ammonia and a few drops of sodium phosphate. Dissolving and reprecipitating is to be avoided, if possible, lest the reprecipitation may not be complete. With water containing ammonia wash the precipitate on the filter two or three times, and then test the washings with nitric acid and silver nitrate.[1]

In case there is a precipitate, wash as before, until, on testing, merely a faint cloudiness is seen. Too frequent washing is inadvisable, hence it is probably better not to wash until the liquid remains perfectly clear on addition of silver nitrate. When the filtration is finished, withdraw the water from the stem of the funnel and place the funnel and contained precipitate in the drying cupboard.

(*d*) **Ignition of Precipitate.**—The ignition of the precipitate needs great care. Soluble phosphates are sometimes added to cotton fabrics to make them non-inflammable, and the solid phosphate in the pores of the filter paper has somewhat the same effect. This makes it necessary to obtain complete combustion, hence the following instructions should be carefully attended to.

Remove the precipitate to glazed paper and burn the filter with all the care exercised with silver chloride. If possible, burn off all the carbon in the wire, but if that is not feasible, allow the ash to fall into a porcelain crucible, put on it a few drops of nitric acid and heat gently. It is well, after putting nitric acid on the charred filter, to tip the crucible so that the

[1] If the washings are not acidified with nitric acid, silver nitrate will not give a precipitate, since silver chloride is soluble in ammonia and the absence of a precipitate would not prove that all of the chloride is washed out.

phosphate dissolved in the acid may be drained away from the carbon. As the acid is evaporated, the white phosphate left behind can be seen in the crucible, and the carbon having been largely freed from phosphate, can be more readily burned. The nitric acid helps to oxidise the carbon, and if one treatment is not successful, repeat the operation. So far, the heating should not be strong at any stage, as there is the possibility of the precipitate fusing and enclosing the carbon particles, which are then doubly difficult to oxidise. When the ash is burned white, add the main body of the precipitate and heat gently.

The equation

$$2(MgNH_4PO_4.6H_2O) = Mg_2P_2O_7 + 2NH_3 + 13H_2O$$

shows what a large amount of volatile matter, ammonia and steam is given off and the danger of spurting that would be caused by rapid heating. Besides this, with too high temperature, ammonia is liable to act on the phosphate and produce phosphide, which is not what is wanted. It is because of the possibility of forming phosphide, which acts on platinum, that a porcelain crucible is recommended. Keep the lid on the crucible, except when examining, to see if the operation is progressing favourably. If vapour is coming off, or a smell of ammonia is noticed when the nose is held over the open crucible, the burner being removed from beneath it for a moment, the temperature is high enough. Allow the heating to go on at this temperature till the water and ammonia are driven off, occasionally removing the burner, in order to allow air to enter the crucible. Do not heat above medium redness before the mass has become white, or it may fuse to some extent. If the mass remains dark, allow to cool, add nitric acid and heat cautiously. After the residue has become white, a final heating on the blast for a few minutes is advisable.

(*e*) **Calculation of Result.**—If the determination has been carried out successfully, the residue in the crucible after ignition will be magnesium pyrophosphate, and the quantity of magnesium oxide can be easily calculated. Students not infrequently make a mistake in the calculation. The quantity of magnesia in magnesium phosphate, $Mg_2P_2O_7$, is of course represented by 2MgO, but sometimes beginners, who wrongly

use symbols instead of names for chemical compounds, calculate the quantity of magnesia as MgO and, hence, get a result only half of what it should be. Of course, the calculation could be made in terms of magnesium instead of magnesia, but in the analysis of rocks the percentage of the oxides of the metals is usually given, and the same procedure is here adopted, and the composition of magnesium sulphate is calculated in terms of magnesia and sulphur trioxide, or sulphuric anhydride.

2. **SULPHUR TRIOXIDE.** (TIME, SIX HOURS.) — The determining of sulphuric anhydride is the converse of the determining of barium by sulphuric acid, but it is open to some errors, which are not likely to occur in the latter case. The precipitate of barium sulphate is liable to carry down other substances with it. Owing to this tendency, it was maintained by a noted chemist more than a century ago, that barium sulphate did not always have the same composition, and the validity of the law of definite proportions was not admitted by him for several years. It was finally proved that different impurities mixed with barium sulphate accounted for the seeming inconstancy of composition.

In the pure barium salt, the addition of sulphuric acid can bring no impurity into the precipitate, which would not volatilise on ignition, except some of the barium salt itself, and if any of that should be carried down, it can be changed into sulphate in the crucible by addition of strong sulphuric acid. Even if the barium salt is not pure, the sulphate produced by the addition of sulphuric acid is not likely to be so contaminated as when barium chloride is added to a sulphate.

When a sulphate is precipitated, as barium sulphate by the addition of barium chloride, the barium sulphate is liable to carry down with it some barium chloride. Nitrates also are specially liable to be carried down, and hence, if possible, no nitric acid or nitrates should be present. If the precipitation is to be made from magnesium sulphate or from alkaline sulphates containing no nitrate, the following precautions will be sufficient for a fair approximation. It is important that all of the solutions should be very dilute and should be hot. Though in the description given here only one determination is followed through, two lots at least should be weighed out

at the beginning and at each stage of precipitation, filtration, and ignition, after one is finished, the other should be proceeded with.

(*a*) **Precipitation.**—Weigh out about 0·3 grm. of magnesium sulphate into a 600 c.c. beaker; add 300 c.c. of boiling water, and a few drops of hydrochloric acid. Heat to boiling, and after removing the flame add very slowly and with continuous stirring, a hot dilute solution of barium chloride. If the barium chloride in the bottle is 10 per cent., about 2 or 3 c.c. more than the calculated amount should be diluted with five times its volume of water, the whole heated and added so slowly that it will take nearly five minutes to add the required amount. The method of calculating how much barium chloride is required has been given already in the general directions (p. 22).

The object in view is to cause the precipitate to form slowly in fine crystals which will afterwards grow, but which will not carry down so much foreign salts as if the solutions were concentrated.

Boil the liquid in the beaker, stirring all the time, so that the precipitate will not settle and cause bumping. As was said under the heading of barium, if, in spite of all the care taken in stirring, there is danger of loss by bumping, the boiling should be stopped though heating may be continued without stirring in the steam or water bath or on the steam plate. After boiling has gone on for about five minutes allow the precipitate to settle and test by adding a little dilute barium chloride solution to see whether the precipitation is complete. If it is not, add more barium chloride, in the same manner as before, till the test shows that enough has been added and then set aside over night, preferably in a warm place, but not where it is hot enough to perceptibly evaporate the liquid.

(*b*) **Filtration.**—The filtration is carried out in the manner described under barium, but even more care must be taken in the washing by decantation. From 50 to 100 c.c. of boiling water and a few drops of hydrochloric acid should be added to the precipitate, the whole heated for a minute or two with stirring, and then, after the precipitate has settled, the clear supernatant liquid poured through the filter. This operation should be repeated three or four times before the

main body of the precipitate is brought upon the filter. Do not neglect any of the precautions mentioned in the earlier chapter, such as seeing that the main filtrate has run through clear and that it is removed before washing is begun, and that during washing the top of the filter paper is thoroughly washed either by completely filling the filter with water or by squirting a stream of water all round the top. Do not neglect to allow *all* of the water to run out of the filter each time between the washings. If the liquid has not all been allowed to run out before water is added again, the precipitate is being washed not with pure water, but with a dilute solution of what one wishes to wash out.

(*c*) **Ignition of Precipitate.**—The ignition of the precipitate is to be carried out as described in the previous chapter, and the calculation as in Chapter III.

The time required is about six hours for the duplicate analysis, as in the case of determining barium : two hours for weighing out the salt and precipitating, two hours for filtration, and two hours for ignition. During this last stage it may be possible to employ the vacant time in preparation for some other determination. The time required for the determination of magnesia is also about six hours, the precipitation does not require so much time but the ignition requires more.

3. **WATER.**—Crystallised magnesium sulphate contains water of crystallisation which may be determined in the same way as the water of crystallisation of barium chloride, but greater care must be taken not to allow the temperature to become too high since sulphuric anyhdride may be driven off. Since a porcelain crucible is less likely to be over-heated than a platinum one, the former should be used. The lid should be kept on.

Appendix

In connection with the determination of magnesium, a general consideration of phosphoric acid and the phosphates is interesting because explaining the errors liable to creep into the analysis.

Phosphoric anhydride, P_2O_5, forms, by combining with water, three distinct acids with different chemical reactions. They are :—

Orthophosphoric acid ($3H_2O$, P_2O_5 or H_3PO_4).
Pyrophosphoric acid ($2H_2O$, P_2O_5 or $H_4P_2O_7$).
Metaphosphoric acid (H_2O, P_2O_5 or HPO_3).

To these acids there are corresponding salts.[1]

Orthophosphoric acid, the most important of these acids, is usually called phosphoric acid and the principal natural phosphates are derived from it. In the normal phosphates, hydrogen is entirely replaced by a metal. The ordinary salts of silver, calcium and aluminium have the composition indicated by the formulæ Ag_3PO_4, $Ca_3(PO_4)_2AlPO_4$. The ordinary sodium phosphate does not, however, correspond to the formula Na_3PO_4, but to Na_2HPO_4, which though acid in formula is neutral to litmus. When the normal phosphate Na_3PO_4 is dissolved in water, hydrolysis takes place, as represented by the equation

$$Na_3PO_4 + H_2O = Na_2HPO_4 + NaOH,$$

and the caustic soda produced renders the solution alkaline. There is a third salt, NaH_2PO_4, which is acid to litmus.

Not only the normal sodium phosphate, but the others as well, when added to a soluble silver salt such as the nitrate tend to form the normal silver phosphate Ag_3PO_4 and not the salts corresponding to the formulæ Ag_2HPO_4 or AgH_2PO_4. It will be seen, however, from the equation

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$$

that the resulting liquid is acid. Silver phosphate is soluble in acid, hence the phosphate is not completely precipitated. When the acid is neutralised by ammonia silver phosphate is more completely precipitated, but on further addition of ammonia it re-dissolves.

In the case of aluminium or calcium salts the precipitate is chiefly if not entirely the normal phosphate as is the case with silver, and the addition of ammonia makes the precipitation complete, since the phosphate is not soluble in excess of ammonia and the compounds thus produced have the formulæ $AlPO_4$ and $Ca_3(PO_4)_2$. With magnesium, however, if ammonia is present the precipitate is not mainly tri-magnesium phosphate, $Mg_3(PO_4)_2$, but magnesium ammonium phosphate, $MgNH_4PO_4$.

[1] There are a number of metaphosphates whose structure is more complicated than that indicated above, but they may be neglected.

The conditions most suitable to the formation of this precipitate have usually been considered to be the presence of ammonium chloride and ammonia in the solution of the magnesium salt. But in the presence of excess of ammonia the reaction represented by the following equation :—

$$MgSO_4 + 4NH_4OH + 2Na_2HPO_4 = Mg(NH_4)_4(PO_4)_2 + Na_2SO_4 + 2NaOH$$

is possible and probably takes place to a certain extent. The presence of a large excess of phosphate and of ammonium chloride contribute to the same result.

It might be thought that since all of the ammonia is driven off on ignition the presence of more or less ammonia in the precipitate would not matter. It is therefore interesting to consider the effect of heat upon different phosphates.

When orthophosphoric acid is heated to a certain temperature it loses water and becomes pyrophosphoric acid :—

$$2H_3PO_4 = H_2O + H_4P_2O_7.$$

When heated sufficiently pyrophosphoric acid is further changed to metaphosphoric acid :—

$$H_4P_2O_7 = H_2O + 2HPO_3.$$

It is impossible to drive off the remainder of the water and form phosphoric anhydride, but metaphosphoric acid may be volatilised to a certain extent by an intense white heat.

A tri-basic phosphate like Na_3PO_4 on being heated remains unchanged, but if the phosphate contains hydrogen, as di-sodium hydrogen phosphate or sodium di-hydrogen phosphate the hydrogen goes off with the corresponding amount of oxygen leaving pyrophosphate or metaphosphate :—

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7$$
$$NaH_2PO_4 = H_2O + NaPO_3.$$

If the phosphate contains ammonia it also is volatilised; microcosmic salt decomposes as follows :—

$$NaHNH_4PO_4 = H_2O + NH_3 + NaPO_3.$$

If the magnesium ammonium phosphate has the composition usually assigned to it, it decomposes according to the equation

$$2MgNH_4PO_4 = H_2O + 2NH_3 + Mg_2P_2O_7,$$

pyrophosphate being thus formed, but if the tri-magnesium

phosphate, $Mg_3(PO_4)_2$ is present it is unchanged while the magnesium ammonium phosphate whose formula is $Mg(NH_4)_4(PO_4)_2$ is decomposed as follows :—

$$Mg(NH_4)_4(PO_4)_2 = 2H_2O + 4NH_3 + Mg(PO_3)_2.$$

The proportion of magnesia, MgO, is evidently different in the three compounds $Mg(PO_3)_2$, $Mg_2P_2O_7$ and $Mg_3(PO_4)_2$, and if the calculation is made on the assumption that the residue on ignition is $Mg_2P_2O_7$, while it is really one of the others, an error is involved. The presence of metaphosphate makes the calculated amount of magnesia too high, and the presence of orthophosphate makes it too low. Since these two errors tend to counterbalance it is possible that the results actually obtained in analysis are nearly accurate, not because the residue is uniform, but because of its counterbalancing variations.

Magnesium metaphosphate is said to be decomposed by the high temperature of the blast, phosphoric anhydride being volatilised and magnesium pyrophosphate being left behind :—

$$2Mg(PO_3)_2 = P_2O_5 + Mg_2P_2O_7,$$

hence the advice sometimes given to ignite for a few minutes on the blast. This advice assumes that the presence of metaphosphate is more likely than of orthophosphate.

A method suggested to ensure the formation of the required magnesium ammonium phosphate is to use microcosmic salt, $NaHNH_4PO_4$, instead of sodium phosphate as the precipitating reagent. Microcosmic salt contains just the requisite amount of ammonium, hence no ammonia is added till after the precipitation is as complete as possible. The reaction does not run to completion because of the acid formed, indicated by the formula $NaHSO_4$ in the equation

$$MgSO_4 + NaHNH_4PO_4 = MgNH_4PO_4 + NaHSO_4.$$

If, however, the mixture is boiled for five minutes, about nine-tenths of the magnesia is precipitated and addition of a small quantity of ammonia precipitates the rest.

The operation is carried out as follows : To a hot solution of magnesium salt add a solution of microcosmic salt and boil for five minutes with constant stirring ; add ammonia drop by drop till there is a faint smell of ammonia. Set the beaker aside over night and carry out the rest of the operation as already given, except that Gooch, who recommends this method, says that the wash water should contain only a very little ammonia.

Students who are beginning an extended course in Quantitative Analysis may find it advisable to try both methods and see which gives the best results. Often beginners find their results indecisive because their errors of manipulation are greater than the errors of the method. The error of the ordinary method is of the order of a few tenths of a per cent.

CHAPTER VII

CALCIUM CARBONATE

1. **CARBON DIOXIDE.** (TIME, TWO HOURS.)—Calcium carbonate gives off carbon dioxide when strongly heated, and thus the amount of carbon dioxide can be determined by the loss on simple ignition, just as the water in barium chloride can be determined by ignition. It is evident that if the calcium carbonate contains any moisture, water would be driven off as well as carbon dioxide. By heating at a temperature of 100 to 110° C. this hygroscopic moisture may be driven off without loss of carbon dioxide and the dried material may be afterwards ignited. Assuming that it is not desired to distinguish between moisture and carbon dioxide, but that the determination is intended merely as a check upon the amount of lime found by precipitation (the two adding to 100 per cent.), the determination may be made as follows :—

Into a weighed platinum crucible put some calcium carbonate and weigh again. Then with the cover on the crucible heat gently for a minute or two with a Bunsen burner, and then with the blast directed slantingly against the lower part of the crucible for five minutes. Remove the crucible with contents to the desiccator and weigh as soon as it is cold. Heat again, as before, for five minutes and weigh once more. If the weight is not constant, repeat the operation until it is.

When calcium carbonate is heated in a closed space the carbonate is decomposed only until a certain pressure of carbon dioxide is reached, which is different for each temperature, after which equilibrium is maintained, calcium carbonate, calcium oxide and carbon dioxide remaining unchanged in the presence of each other. In the burning of lime in a lime kiln a current of air or of steam is used to drive away the carbon dioxide as soon as formed and thus enable the decomposition to be brought to completion. Upon the same principle it is sometimes recommended to lay the crucible on its side

and place the lid against it in a slanting position so that a current of air may pass over the carbonate while it is being heated, but this is usually unnecessary.[1]

The crucible may be placed upright with the cover upon it, and if the blast is directed slantingly against the lower part of the crucible, so that the mouth of the crucible is free from the carbon dioxide produced by the combustion, the carbon dioxide of the carbonate will escape. There is no great object in long heating, five minutes with a good blast will probably be enough, and even platinum may be affected by very long heating. It will probably be found that after the second heating for five minutes the weight has not changed by more than the allowable amount. When the weight has become constant with the crucible upright and the lid upon it, try laying the crucible on its side with the lid laid against it, and see whether there is any further loss. If so, repeat till the weight is constant. Take care, however, that the loss is not due to little particles of the powder being blown away. A continual small loss each time may be due to loss in the platinum, and the crucible should in that case be weighed again after the lime is removed.

The calcium oxide in the crucible is so hygroscopic that even in the desiccator it may absorb moisture if allowed to stay longer than is required for cooling, and it is specially necessary to weigh as rapidly as possible. This is a case where trying to adjust the rider to the exact weight rather than calculating the weight from the swings is likely to be inaccurate. In all weighings except the first place the weights on the balance before removing the crucible from the desiccator. The time required for adjusting the rider sufficiently to enable the swings to be taken is all that will be required for getting the exact weight.

2. **CALCIUM OXIDE.** (TIME, SIX HOURS.)—(*a*) **General Considerations.**—The most suitable form in which to precipitate calcium is the oxalate. In the ordinary course of analysis of a rock, the main substances left in solution with

[1] The strongest flame of the Bunsen burner may be used if the blast is not convenient, but in that case the crucible is better to be laid on its side, and the heating may be for fifteen or twenty minutes.

calcium salts are magnesium salts and salts of the alkalies. In the analysis of calcium carbonate, the first step is to get the carbonate into solution. It does not dissolve in water, but it is readily soluble in dilute hydrochloric acid, giving calcium chloride, and carbon dioxide, which goes off as a gas, especially when the solution is heated. The solution is now acid, and calcium oxalate is soluble in acid. If the solution is made, alkaline with ammonia, and then ammonium oxalate is added, calcium oxalate will be thrown down. This method is satisfactory if there is nothing present except ammonium salts, but though magnesium oxalate is soluble, it is liable to be carried down in the precipitate of calcium oxalate, especially if the solution is alkaline and there is not an excess of ammonium oxalate. Hence, instead of making the solution alkaline and adding ammonium oxalate, it is better to add oxalic acid to the acid solution, and then to add ammonia gradually. Most of the calcium oxalate thus forms in a slightly acid solution, which tends to keep it free from magnesium. Since the oxalic acid is in excess of what is required, the calcium is precipitated either in an acid solution or where there is excess of ammonium oxalate. In accordance with the above explanation, proceed as follows :—

(*b*) **Precipitation.**—Weigh out into a 450 c.c. beaker (with, of course, a duplicate) about 0·4 gramme of calcium carbonate. Pour in about 20 c.c. of cold water. Cover with a cover glass, and lifting up the cover at one side, pour in carefully a little hydrochloric acid. Effervescence will at once take place. If the substance does not all dissolve in a few minutes, add a little more acid and heat, with the cover still on the beaker. If there is a residue which does not effervesce, it is probably silica or silicate, and should be filtered off, washed with hot water, ignited and weighed (since its weight will be required to make up the 100 per cent.). The probability is that there will be no residue if the carbonate is artificial and not mineral, in which case wash off the cover glass into the beaker with a stream of hot water from the wash bottle, and add boiling water to the solution till the beaker is nearly half full. Then add enough solid oxalic acid to be slightly more than equivalent to the calcium present. If there is a precipitate formed, it is because the liquid is not acid enough to

keep the calcium oxalate entirely in solution, the action of oxalic acid and calcium chloride being a reversible reaction the direction of which depends upon the relative amounts of the various substances present. In case there is a precipitate, add hydrochloric acid slowly, with stirring, till the precipitate is dissolved. Then add, very slowly, dilute ammonia. As soon as the precipitate begins to form, add ammonia, a drop at a time, from a pipette. Some chemists advocate adding the ammonia so slowly that it will take half an hour before enough has been added to complete the precipitation. Probably five minutes will be sufficient. Add ammonia till the liquid smells faintly. Then add about 5 c.c. of a saturated solution of ammonium oxalate which contains about 10 per cent. of the salt, boil for a couple of minutes, and allow to stand. If the oxalate can be filtered after standing four hours, there is less likelihood of magnesium being carried down. If this is not possible, allow to stand until the next laboratory attendance.

Calcium oxalate is liable to run through the filter. In order to coagulate it and counteract this tendency, sometimes a solution of ammonium alum is added, containing such an amount of the salt that on ignition it will give 1 milligramme of alumina, Al_2O_3. Ammonium alum has the formula $(NH_4)_2SO_4$, $Al_2(SO_4)_3$, $24H_2O$, and from this the calculation can be made. Of course, from the final weight after ignition, this weight of 1 milligramme must be deducted. The addition of alum is not recommended, unless the first precipitate runs through the filter, in which case it may be added to the duplicate. If the following directions are carefully followed, the probability is that the filtration will go satisfactorily.

(*c*) **Filtration.**—Heat the beaker in the water or steam bath, pour off the clear liquid through a filter without disturbing the precipitate and, if the filtrate is perfectly clear, remove it. Wash the precipitate by decantation two or three times with boiling water, containing about 1 per cent. of ammonium oxalate solution. Then clean out the beaker as usual, adding a few drops of ammonium oxalate solution to the water each time, or use boiling water, containing about 1 per cent. of ammonium oxalate. If some of the calcium oxalate sticks to the beaker, so that it cannot be removed, dissolve with a little dilute hydrochloric acid and reprecipitate with ammonia,

adding a few drops of ammonium oxalate to make the precipitation complete. Wash the precipitate on the filter, either with boiling water, or with a hot, very dilute solution of ammonium oxalate till all chloride is washed out. Hot water is said to have a slight solvent effect on calcium oxalate. Hence the suggestion to use ammonium oxalate in the water.

(*d*) **Ignition.**—The precipitate is not weighed as calcium oxalate which is too readily decomposed. It is sometimes weighed in the form of carbonate, but this is not usual. It is more frequently changed either to oxide or to sulphate. It is most commonly changed to oxide, if a good blast is available. In this case the precipitate may be burned either wet or dry. If it is burned wet, carry out the ignition in the usual manner, but when the filter is completely burned, place the crucible upright with the cover on and heat with the blast in a slanting direction, as already described in this chapter. It must be borne in mind that calcium oxalate on being heated gives off more than half its weight as the gases carbon monoxide and carbon dioxide. Hence the greater part of these gases should be driven off at as low a temperature as possible, so that the solid may not be thrown out of the crucible. The carbon monoxide may be seen burning, and this burning should be as quiet as possible, only after flame ceases should the blast be applied. Five minutes' heating on the blast is sufficient. Cool and weigh rapidly. Blast again for five minutes and weigh to constant weight. Under these conditions there is little danger of the residue not being completely changed to oxide. If the precipitate is to be weighed as sulphate it is better to burn it dry. Remove the precipitate to glazed paper, burn the filter in a wire, allow the ash to fall into the crucible, and if the carbon is not entirely burned already, heat the crucible till it is all gone. Then when the crucible is cold, add the main precipitate, put upon it a few drops of dilute sulphuric acid containing more than enough of the acid to decompose the oxalate and change it all to sulphate. Heat gently to drive off the water and free acid. This can perhaps be most readily done by placing the crucible with the cover slightly open on a triangle or ring in an iron cone the shape of a large crucible, the crucible being separated from the cone by a distance of nearly a centimetre. Even the full flame of

the Bunsen playing upon the cone will probably not be too hot, but if it is, regulate the flame accordingly. When the fumes of sulphur trioxide have ceased to come off, heat the crucible for a minute or two to a dull red heat in the direct flame. Too high a temperature would decompose the sulphate. After cooling in the desiccator and weighing, put another drop of sulphuric acid upon the precipitate and heat again as before. If the weight has changed more than the allowable amount, repeat the process. If ammonium alum has been added to coagulate the calcium oxalate, treatment with sulphuric acid is not recommended, for although aluminium sulphate on ignition changes to alumina, Al_2O_3, yet, when mixed with a large quantity of calcium sulphate and not very strongly heated it may not be entirely decomposed, and, on the other hand, one cannot assume that no decomposition would take place.

When the oxalate is ignited on the blast, the residue is the required calcium oxide; when it is changed into sulphate, the amount of oxide can be calculated, and hence the percentage obtained. All the equations representing the reactions are very easy, and have not been given, but they should be written in your record book to make it quite clear that you understand all the processes involved. The time required is about six hours for this determination also, but probably the determination of the carbon dioxide can be so fitted in with that of the calcium oxide that the two will take little, if any, longer than six hours.

CHAPTER VIII

CEMENT, LIMESTONE, CLAY

(TIME, TWENTY-FIVE HOURS.)

1. **GENERAL CONSIDERATIONS.**—The analysis of cement well exemplifies the statement made in the first chapter that no precipitate is perfectly insoluble and no method of separation is absolutely accurate.

The substances usually determined are silica, iron and alumina, lime, and magnesia. In the ordinary separation the silica is liable to be contaminated, chiefly with alumina, while some of it is not precipitated; the alumina and iron precipitate contains most of the silica which escaped precipitation in the proper place, also some lime and magnesia; the lime may contain some alumina which was left in solution when the main portion was precipitated, along with some magnesia carried down as oxalate with it, and the magnesia will probably be mixed with any of the others that have escaped precipitation before. It will be seen that these errors more or less counterbalance each other, and it may happen that the results obtained may not be more than $\frac{1}{2}$ per cent. from the real composition.

2. **PROCESS.**—The process to be described is confessedly a rough one, of the commercial type; after it has been described the refinements which make a more accurate method of analysis will be touched upon.

(*a*) **Moisture, etc.**—Cement contains, in addition to the constituents above-mentioned, usually hygroscopic moisture, carbon dioxide, and sulphuric anhydride; sometimes alkalies and chlorine. The moisture may be determined by heating for an hour at 100° to 110° C. in an air bath whose temperature can be regulated; the loss on ignition (in which a gramme is ordinarily used) consists mainly of water and carbon dioxide though a little of the alkalies, and of sulphuric anhydride may be driven off. The ignition takes five minutes on the Bunsen, starting first with a low flame and gradually increasing the temperature, and then ten or fifteen minutes on the blast.

The determination of alkalies is beyond the scope of this book, nor will the determination of sulphur trioxide or chlorine be specially discussed.

(*b*) **Silica.**—When cement is treated with hydrochloric acid of the proper strength, nearly all of it dissolves, and when evaporated to dryness most of the silica becomes insoluble in water or dilute acid. Sometimes heating the dried mass to 120° to 130° C. is recommended, but there seems to be little, if any, advantage in heating to a higher temperature than can be obtained in the steam bath.

In determining silica in cement proceed as follows :—

Put into a porcelain dish or casserole about 0·5 gramme of cement and moisten it with sufficient water to keep it from lumping. Probably this will be about 5 c.c. Then add 5 or 10 c.c. of strong hydrochloric acid, heat gently and stir till the mass dissolves, then evaporate to dryness on a steam bath. Moisten the residue with 5 to 10 c.c. (preferably the smaller quantity in most cases) of strong hydrochloric acid, allow to stand for a few minutes, then add an equal quantity of water, cover the dish and place it on the bath for ten minutes longer, after which add 40 to 50 c.c. of hot water and allow to stand long enough to settle. Filter the clear liquid, leaving in the dish most of the precipitate which will usually be in a coarse condition. Break down the lumps with a glass rod, wash two or three times by decantation with about 5 c.c. of hot water containing approximately 1 c.c. of strong hydrochloric acid to 10 of water, transfer the precipitate to the filter, and if there is much iron wash with cold water till it is pretty well washed out, and then finish washing with hot water. The silica precipitate is so liable to retain salts from the solution that special care must be taken that they are washed out.

When it is thought that the washing should be complete, collect about 3 c.c. as it comes from the funnel and test for chloride with silver nitrate. Hot water containing no acid might convert the ferric salt into a basic chloride which would stick to the silica, hence the advice to use cold water.

Transfer the filter with precipitate to the platinum crucible and burn it in the usual manner. Silica precipitated in this way holds the last traces of moisture very pertinaciously, and

the crucible, with the cover on, must be heated with a strong blast for half an hour, and after weighing, for fifteen minutes, and to constant weight.

The precipitate of silica is not likely to be carried through the filter by the washing, so it is probably not necessary to change the dish to receive the washings. But it is necessary that none of the filtrate or washings should be lost and hence care must be taken that there is no splashing, as the liquid drops from the funnel. This can be provided for by having the stem of the funnel touch the side of the vessel receiving the filtrate.

(*c*) **Iron and Alumina.**—From the filtrate just mentioned there is now to be precipitated ferric and aluminium hydroxide. For this purpose it would be better to have the solution diluted to about 250 c.c., but, on the other hand, such a large quantity of liquid would give a very large filtrate from which to make the further precipitations. Moreover it is probably better to precipitate the iron and alumina in a porcelain dish (and those supplied in a quantitative set of apparatus are usually not very large) rather than in a glass beaker, because the glass is liable to be acted upon by the ammonia used in precipitation. However, Jena or Resistance glass is little affected. We shall assume that the filtrate from the silica is in a porcelain dish or casserole and is between 100 and 150 c.c. in volume. Probably the iron is already all in the ferric condition, but if not it must be oxidised, because ferrous hydroxide, which would be formed by the action of ammonia on the ferrous chloride present, is partially soluble in ammonia in somewhat the same way as nickel and cobalt and zinc hydroxide are soluble. Any ordinary oxidising agent which does not bring in an undesirable impurity may be used, for instance, nitric acid or bromine water or hydrogen peroxide. Hydrogen peroxide sometimes contains phosphoric acid, in which case it should not be employed. Only a very small amount of any of the reagents will be needed.

Ammonia precipitates iron and alumina, and it is generally stated that any considerable excess of ammonia redissolves some of the alumina, though this is denied on good authority. There is no doubt that ammonia is liable to absorb carbon dioxide from the air, and ammonium carbonate tends to

precipitate calcium carbonate, hence care must be taken not to allow the liquid to stand any longer than necessary.

In accordance with the above considerations, proceed as follows :—

To the filtrate from the silica in a porcelain casserole add a drop or two of nitric acid or of bromine water, boil, add slightly diluted ammonia solution slowly till the precipitate begins to form, afterwards add the ammonia drop by drop till no more precipitate is produced, then boil, taking care that there is no spurting. The boiling need not be long, since a great excess of ammonia has not been added.

Since the precipitate thus formed is gelatinous and liable to clog the filter, the washing should be mainly by decantation. Pour off the clear liquid, wash several times by decantation with boiling water, either pure or containing a little ammonium nitrate, remove the precipitate to a fairly large filter (7 cm. or 9 cm. diameter) folded as directed on the footnote on p. 25, and wash on the filter till all the chloride is removed, as may be tested for by addition of silver nitrate and nitric acid.

The removal of the precipitate from the porcelain dish may give trouble unless the finger is used for the purpose. Clean the little finger very carefully, especially under the nail, finally washing it off with distilled water ; then adding a little water, rub out the porcelain dish with the finger, bringing the precipitate into the filter, using the finger just as a glass rod is used. Repeat the operation until every particle of the precipitate is removed. Burn the precipitate wet, or if the filter is too large to put into the crucible in that condition, allow it to dry till the precipitate has shrunken enough to permit the filter to be rolled up sufficiently. Finally heat the precipitate over the blast, taking care that the reducing gases from the flame do not enter and that air will have access so that the iron will be in the condition of ferric oxide and not partially reduced. The addition of macerated filter paper (obtained by tearing a small filter into shreds), just before or just after the precipitation of the iron and alumina by ammonia, is recommended because it will make the precipitate powdery when it is burned and thus easily oxidisable. The blast is used for the same reason as with silica.

(*d*) **Calcium.**—As the precipitated ferric hydroxide and

aluminium hydroxide needs a good deal of washing, the combined filtrate and washings will probably amount to 300 c.c. If not, dilute to that volume, in a 600-c.c. beaker for the precipitation of calcium as oxalate. As was stated in the last chapter, the precipitation is best made from an acid solution by addition of oxalic acid and afterwards very slowly of ammonia. Since a large quantity of ammonium salts is a disadvantage in the subsequent precipitation of magnesium, be careful not to add too much oxalic acid or ammonium oxalate; though on the other hand, remember that it is necessary to add a considerable excess over that actually required for the precipitation of the calcium oxalate. Follow out the process as given in the last chapter. Since the precipitate is liable to run through the filter on being washed, keep the washing separate from the clear filtrate. It may be well to evaporate them separately.

(*e*) **Magnesium.**—Evaporate till the combined filtrate and washings are reduced to 200 c.c. If on cooling salts of ammonia do not crystallise out, add about 10 c.c. of a 10 per cent. solution of sodium phosphate or of microcosmic salt; add ammonia slowly, stirring vigorously without touching the sides of the beaker. Allow to stand over night or longer before filtering.

If ammonium salts separate out when the liquid which has been evaporated to 200 c.c. is cooled, add strong nitric acid and continue the evaporation. Ammonium chloride is decomposed in some such way as that represented by the equation

$$NH_4Cl + HNO_3 = HCl + 2H_2O + N_2O.$$

The hydrochloric acid produced may, along with nitric acid, give chlorine and brown fumes of nitrogen peroxide. The amount of nitric acid required will probably be found to be greater than would be calculated from the above equation, and several successive additions may be required. It may be well after the liquid has evaporated to dryness to heat the dry mass till fumes of ammonium salts cease to be given off. Nitric acid helps to oxidise ammonium oxalate, and so it is decomposed as well as ammonium chloride.

After the ammonium salts have been decomposed, take up the residue with a little hydrochloric acid and water, filter off

any silica or organic matter that may be undissolved, burn the filter and add the weight of the residue, if any, thus obtained to the weight of the silica already determined.

To the filtrate, which should not amount to more than 75 c.c. or 100 c.c., add sodium phosphate or microcosmic salt, and afterwards ammonia drop by drop till the liquid distinctly smells of ammonia. Keep stirring vigorously all the time and even for three or four minutes after the precipitate seems to be completely formed. Allow to stand over night. Filter as described in Chapter VI. Care must be taken in washing the magnesium ammonium phosphate. Do not rely on the amount of washing required in the simple precipitation, but test the washings. This is especially necessary if the precipitation has been made without the removal of ammonium oxalate, for on the addition of the sodium phosphate or microcosmic salt sodium oxalate is formed which clings very tenaciously to the magnesium precipitate. Test the washings either for chloride with silver nitrate and nitric acid or for oxalate with calcium chloride. The ignition is carried out in the method given on p. 46.

3. **REFINEMENTS IN THE PROCESS.**—As already stated, none of the precipitates obtained in the manner described above are quite pure, and in order to get more accurate results, the following measures are to be adopted: After filtering the silica, evaporate the filtrate to dryness, take up the residue as before, with hydrochloric acid, and filter off the small amount of silica which remains undissolved. Many of the text-books on quantitative analysis recommend evaporating the cement to dryness with hydrochloric acid, adding acid, and evaporating to dryness a second time before taking up with acid and water and filtering. It has been proved that the second evaporation is of little, if any value, as the silica present tends to recombine with the bases, especially with magnesia. But if the main part of the silica is filtered off and the filtrate evaporated to dryness, then the small quantity of silica remaining is, for the most part, separated out.

Hydrofluoric acid changes silica into silicon fluoride, which is gaseous, but acts slightly, if at all, upon alumina. Hence, if the silica precipitate is contaminated with alumina or iron, as

is probable, the amount of silica and of the impurity may be determined. After igniting and weighing the combined precipitate of silica, add to the material in the crucible a cubic centimetre, or less, of water, containing a drop or two of strong sulphuric acid and a few cubic centimetres of hydrofluoric acid and heat, as described in the determination of calcium as sulphate (p. 59).[1]

After the sulphuric acid has been driven off, heat the residue for a minute in the blast. The presence of sulphuric acid assists in driving off the silicon fluoride and prevents the formation of fluoride of iron or aluminium. The sulphates of these metals are formed during the evaporation, but are decomposed at the high temperature, forming ferric oxide and aluminium oxide. The difference between the weights before and after treatment with hydrofluoric acid gives the silica, and the weight of the residue left behind should be added to that of the oxides of iron and aluminium found later.

The precipitate of ferric hydroxide and aluminium hydroxide is liable to retain a little calcium and magnesium. To get rid of these, after washing the precipitate in the casserole once or twice, by decantation, and also the precipitate on the filter, dissolve the latter in dilute hot nitric acid, allowing the solution to run into the casserole. The solution of the precipitate on the filter can be best effected by dropping acid on the precipitate, and then squirting water upon it. In this way the precipitate gets stirred up, and the soluble part is washed through with water, instead of with acid. Alternately use acid and water, until the precipitate is dissolved, and then wash thoroughly with water. If the precipitate in the casserole is not all dissolved by this time, heat, and if necessary, add more acid, and after diluting to 100 c.c. precipitate, as before, with ammonia, and wash the precipitate with hot water containing a little ammonium nitrate. By dissolving the precipitated hydroxides in nitric acid instead of hydrochloric, less washing is needed after the next precipitation, as there is

[1] Hydrofluoric acid produces very severe burns, and the fumes are very irritating and poisonous, so that not only must the operation be carried on in the draught cupboard, but great care must be taken that none of the liquid gets upon the hands. If it does wash *very thoroughly* with water. The acid sticks much more persistently than one would naturally expect.

little present but ammonium nitrate, which need not be removed, as it disappears on ignition, its presence being useful, rather than otherwise, as it helps to oxidise the iron. Ammonium chloride, if not all washed out, would, during the ignition, produce ferric chloride, which would volatilise, and so be lost. The filtrate from this precipitation must, naturally, be added to the filtrate containing the main quantity of calcium and magnesium. The object of the second precipitation is to get rid of the small quantity of calcium and magnesium carried down with the precipitated hydroxides. Suppose the first precipitate carries down 2 per cent. of the total calcium, and the second precipitation carries down 2 per cent. of this small amount, it is evident that the second precipitation of iron and alumina would be fairly free from this impurity. The precipitate of iron and alumina is not, however, freed from silica in this way. Its determination is somewhat more difficult, and the student desiring the method is referred to Bulletin 422, U.S. Geological Survey, p. 105.

The precipitate of calcium oxalate is liable to contain magnesium, and for accurate work solution and reprecipitation in a manner similar to that just described is advisable, the reagents being, of course, different. Hydrochloric acid is better than nitric for dissolving the oxalate. As the amount of magnesium in cement is usually small, there is not much necessity for reprecipitation, except in the case of natural cements.

4. **CEMENTS NOT EASILY DISINTEGRATED.**—It should be noted that some cements, especially if old, may not be entirely decomposed by hydrochloric acid. It is well known that some silicates, such as feldspar and mica among minerals, and porcelain and glass among artificial compounds, are almost unattacked by hydrochloric acid, while many of the zoolites and many basic slags, as well as most cements, are decomposed. If a cement cannot be completely disintegrated by the acid, it should be heated in a platinum crucible with half its weight of anhydrous sodium carbonate. Heat at first over a low flame, then for five minutes with the full heat of the Bunsen, and after that for five minutes over the blast. The mixture does not fuse, but it sinters, and the sodium carbonate

so far acts on the cement that it can be disintegrated by acid, after which the analysis proceeds as already described.

5. **CLAY.**—Clay is mainly silicate of alumina, and is far less acted on by acid than is any cement. Heating with half its weight of sodium carbonate does not render it decomposable; it must be heated with eight or ten times its weight.

(*a*) **Fusion.**—Dry some clay at about 110° C., and put ½ gramme of it into a large platinum crucible in which there is somewhat less than 5 grammes of sodium carbonate; mix the clay and the soda with a glass rod, and with a camel's hair brush, brush off into the crucible what sticks to the rod. Sprinkle a little more sodium carbonate upon the mixture in the crucible, heat slowly over the Bunsen, so that there will be no loss by spurting, due to the escape of carbon dioxide set free by the action upon the carbonate of the silica and alumina of the clay. Afterwards heat more strongly, finally over the blast. The extremely basic silicate and aluminate thus formed fuses, and the action should be continued till the fused mass is perfectly quiet, since, so long as there are bubbles of carbon dioxide escaping, the action of the clay upon the carbonate is not complete. When the fusion is finished, cool the crucible and remove the contents to a casserole. A good way to do this is to lay the crucible on its side as soon as the blast is removed, and while the material is still liquid. As soon as it is hard enough not to flow, when the crucible is placed upright, hold the crucible in the tongs and dip it into cold water. The sudden cooling will probably loosen the solid mass. Lest some should be scattered by the contraction, the cover should be on the crucible. The tongs require only a very small opening. When the crucible is cold, take it in the hands, and there will probably be little difficulty in removing the greater part of the contents to a casserole.

(*b*) **Disintegration.**—Put enough water into the casserole to disintegrate the mass, cover it with a glass, dissolve the residue in the crucible with a little dilute hydrochloric acid, and add slowly to the casserole, so that the effervescence will not be too great. If, after all the material is removed from the crucible the effervescence has not ceased in the casserole, add a little more acid to the latter, gently warming if necessary.

When no more gas comes off, squirt off the cover glass into the casserole, and unless you think there is enough excess of acid, add 5 c.c. more and evaporate as before.

(*c*) **Evaporation.**—Alkali salts are liable to "creep," that is, aqueous solutions tend to climb up the sides of the dish. If the heating takes place on a water bath, when the liquid reaches the top of the dish, the steam from the bath is likely to wash it away. This would, naturally, cause loss. To prevent the creeping, it is well to coat the top of the dish inside with a thin film of vaseline and, in any case, the dish should not be set far down in the bath and it should be watched. It is better if the evaporation can be done on a steam plate, where it does not boil. Boiling would cause bumping.

(*d*) **Special Precautions.**—The rest of the operation is much the same as with cement. The presence of the large quantity of alkali salts causes the precipitates to be contaminated by them, and this must be provided against by very careful washing. Their presence also makes the separation of silica more difficult, and it is absolutely necessary to evaporate the second and, perhaps, even a third time. It must be specially noted that double evaporation with acid without filtration between, is of little, if any, value. The silica separated out by the first treatment must be filtered off, the filtrate evaporated again, and the residue thus obtained taken up with acid and water and filtered, to get the rest of the silica.

6. **LIMESTONE.**—The analysis of limestone differs very little from that of cement, except that more dilute acid may be used, and since there is effervescence, care must be taken that nothing is lost. The residue may consist of fine quartz, or of silicates unattacked by acid. Sometimes this is recorded as insoluble residue of silica and silicates, but if the amount of pure silica in the residue is desired, the residue, after being weighed, must be fused with sodium carbonate; the fused mass must be evaporated with hydrochloric acid, taken up with hydrochloric acid and water, and filtered; and the precipitate must be ignited and weighed. The filtrate is added to the main filtrate from the first insoluble residue. The object of weighing the residue before fusion with sodium carbonate is simply as a check, and it is probably not worth while

to heat for more than five minutes on the blast or to weigh more than once. The error will probably be not more than a milligramme or two, and may be less.

7. **ADDITIONAL DETERMINATIONS.** (*a*) **Iron.**—Sometimes in cement it is desired to determine the iron as distinct from the alumina. This may be done in various ways. The combined precipitate of ferric hydroxide and aluminium hydroxide may be dissolved in dilute hydrochloric acid and the solution added to an excess of caustic potash in solution. Ferric hydroxide is precipitated, and the aluminium hydroxide is kept in solution. After filtration, aluminium hydroxide is precipitated from the potash solution, by boiling with excess of ammonium chloride.

The more usual method is, however, to determine the percentage in the same way as iron is determined in an iron ore. Since what is determined in this case is the metal, and what is determined when iron and alumina are obtained in the ordinary course of cement analysis is ferric oxide, the amount of iron found must be multiplied by ten-sevenths, in order to get the ferric oxide, and this percentage subtracted from the percentage of combined ferric and aluminium oxide gives the percentage of the latter.

(*b*) **Sulphate.**—Nearly all cements contain calcium sulphate in the form of gypsum or plaster of Paris put in to retard the setting. The amount ordinarily varies between 1 and 2 per cent., and the method of determining the amount depends upon determining the sulphuric anhydride. Since its amount is small a gramme of cement is used in the determination. The method is much the same as in the case of magnesium sulphate except in the method of getting the material into solution. Also, since the quantity of barium sulphate to be produced is less than in the case of the magnesium salt, a slightly smaller quantity of water may be used.

To a gramme of cement add 10 c.c. of water and stir till the lumps are all broken up, then add 15 c.c. of hydrochloric acid (1·1 specific gravity) and heat till the material is all decomposed and nearly all dissolved. Filter off the small amount of residue, dilute the filtrate to 250 c.c. and heat to boiling. Add 10 c.c. or somewhat less of boiling 10 per cent. barium

chloride solution, probably better diluted with two or three times its volume of water, using the care recommended in the case of magnesium sulphate. As there is only a little sulphate the precipitate is less likely to be contaminated by absorption of other salts. If the operation is carried out in the above manner silica is not liable to be mixed with the barium sulphate precipitate. The precipitate after standing over night, is filtered, ignited and weighed in the usual manner.

8. **NOTES.**—If any material sticks to the crucible and cannot be readily washed out with water, it may be removed in the case of silica with a little hydrofluoric acid, heated, in the case of iron and alumina or of magnesium pyrophosphate, by boiling with dilute hydrochloric acid (equal volumes of strong acid and water), and in the case of barium sulphate, by heating with strong sulphuric acid. Be careful not to put water into the sulphuric acid while it is hot.

The time required for a duplicate analysis of cement done with only one evaporation for silica and with only one precipitation of iron and alumina, of calcium, and of magnesium is about twenty hours. An analysis in which these operations are done twice will require about thirty hours.

CHAPTER IX

COAL

(TIME, FOUR HOURS.)

THE analysis of coal given here is what is called the proximate analysis. It is not a method for determining the exact amounts of carbon and hydrogen which are the principal combustible portions. These are obtained by the process called " ultimate analysis." The proximate analysis does not give a sure test of the character of a coal, but it gives a very fair idea of its nature.

1. **SAMPLING.**—Since one lump of coal may contain little or no stony matter, and another may contain a large amount, it is evident that in testing a carload of coal great care must be taken in sampling. A shovelful is taken from fifteen or twenty representative places in the load and the total weight obtained. By exposure to the air until the coal appears to be dry, the water is evaporated from it and the amount of moisture reckoned in percentage. The dry coal is crushed and quartered till a sample of about 5 lbs. is obtained.[1] This should be crushed more finely and quartered till about ½ lb. is obtained which will pass through a forty mesh seive. One half of this should be put aside in a closely-stoppered bottle in case it should be required, and the other half, after weighing, is dried at 85° to 90° C. and allowed to cool in the air and weighed again. The moisture thus obtained, together with that already determined, gives the water due to wetting by rain or snow, what may be called the external water. Much the same result would be obtained by allowing the coal to lie

[1] In quartering, the sample is thoroughly mixed and spread evenly on a flat surface in approximately a circle. Two lines at right angles are drawn across the sample, two of the quarters opposite each other are taken away, and the other two are more finely crushed, mixed and spread out as before. The operation is repeated till a sample of the required size is obtained.

open to the air for several days. The air dried coal is then quartered till a sample of about 20 grammes is obtained. Usually this sample is ground to 100 mesh, though for some purposes, regarding which the student is referred to special books on coal analysis, it may be best not to grind it so finely. The results obtained in the further analysis depend partly upon the fineness of grinding.

2. **PROXIMATE ANALYSIS.**—The four things determined are moisture, volatile combustible matter, ash, and non-volatile combustible matter, often called fixed carbon. Moisture and volatile matter are determined by loss on heating, ash is determined by direct weighing, and fixed carbon is obtained by deducting the sum of the other three from the total weight of coal. The operations are carried out somewhat arbitrarily, and the results obtained depend upon how closely the directions are followed.

(*a*) **Moisture.**—In an open crucible heat 1 gramme of the coal at a temperature of 104° to 107° C. in an air bath with gas regulator. Cool in the desiccator, and weigh as quickly as possible with the crucible covered so that moisture may not be absorbed from the air. Formerly heating till the weight was constant or began to increase was recommended, but now the standard method is that given above.

(*b*) **Volatile Combustible Matter.**—The standard directions of the Committee on Coal Analysis, appointed by the American Chemical Society, are to use a large platinum crucible of 20 to 30 grammes, and to place it in a platinum triangle. The large crucible allows the coal to be spread in a thin layer on the bottom, and the platinum triangle does not waste so much heat as a clay or porcelain triangle. A 10 gramme crucible may be used and an ordinary triangle, but the triangle should be large enough to just catch the crucible near the top, so that the lower half may be in the direct flame in order that the part containing the coal may be strongly heated. The results will not be exactly the same as if a large crucible and a platinum triangle were used; but duplicates should be fairly concordant. In order to get the highest temperature obtainable with a Bunsen burner use a flame about 25 cm. high and place the platinum crucible containing 1 gramme

of air dried coal just above the inner blue cone. This will be about 8 cm. above the burner, or one-third the height of the flame. The hot flame will in this way completely surround the crucible, which must be covered by a closely fitting lid. Heat for exactly seven minutes. With bituminous coals there will be a considerable escape of gas which will burn with a luminous flame. Probably the lower side of the cover will have a coating of carbon due to volatilised hydrocarbons that have been decomposed. Allow the crucible to cool, partly in the air, but without removing the cover, otherwise some of the carbon will burn away; remove to the desiccator, cool to the temperature of the balance and weigh. As the coal used was only air dried the volatile combustible matter is the total loss minus the moisture already determined.

(*c*) **Ash.**—In order to avoid the necessity of an extra weighing it is customary to use the sample in which the moisture was determined, for determining the ash. It might be thought that after the moisture had been determined the sample might be heated for the volatile combustible matter and that the same sample might afterwards be used for the ash. This was formerly done, but the present method is different. After coal has been strongly heated the carbon is in such a condition as to be difficult to burn. Moreover, if in determining the volatile combustible matter any particles were carried away that would give ash, not only would the combustible matter be too high, but the ash would be too low, whereas if a fresh sample is taken for ash the correct amount of the latter at all events is determined.

After the weighing to determine moisture, lay the crucible on its side in the triangle leaning the cover against it, and heat with a low flame with free access of air. In this way the carbon burns more rapidly than with application of a high temperature. As the burning proceeds it may be advisable to increase the temperature and at the end the blast may be used for a few minutes. But alternating with the strong heating, cooling to allow the mass to absorb oxygen is recommended. A number of heatings and coolings, each lasting about a couple of minutes, is more effective than continual heating for a considerably longer time. After constant weight has been obtained stir the ash with a wire or spatula or knife-

blade, brush it off into the crucible and heat again. Sometimes the ash though apparently burned on the outside, contains carbonaceous matter in the interior. The weight must again be made constant.

(*d*) **Fixed Carbon.**—The fixed carbon is obtained by subtracting the percentage of moisture volatile combustible matter, and ash from 100. This is not quite exact because the ash is not necessarily the exact measure of the inorganic matter. Iron pyrites, for example, is oxidised to ferric oxide, part of the sulphur will have gone off with the volatile matter and part will have remained with the fixed carbon. The error, however, is small and may be neglected.

(3) **ADDITIONAL NOTES.**—The student should consider how far the analysis of coal can be classed under the general methods of analysis mentioned in Chapter II.

The time required is chiefly that needed for the weighings. Usually the air-bath in a laboratory cannot be depended upon to give the constant temperature required, and it should be requlated in the intervals of doing some other work. For instance, in a three-hour attendance, during the first hour or so the bath should be looked at occasionally and adjustment made till the correct temperature is obtained. Too many students waste time in doing nothing else while regulating the bath to constant temperature. If a number of students are analysing coal at the same time it is probable that the bath will be adjusted. If the sample is received ready for analysis two or three hours should be enough for the actual work of the analysis and they should be made up of spare minutes from other more difficult determinations.

CHAPTER X

COPPER

1. **ELECTROLYTIC METHOD.** (TIME, THREE HOURS.)—The easiest and most accurate method for determining copper, if a proper electric current is available, is by electrolysis.

(*a*) **Preparation of the Ore for Electrolysis.**—For this purpose dissolve the finely pulverised ore by the addition of 6 c.c. each of hydrochloric, nitric and sulphuric acid in the order given. The quantity of ore taken varies from ½ gramme with rich ores to 3 or 4 grammes with very poor ores. It is convenient to have the quantities the same in the duplicates, and except with rich ores (say over 20 per cent.), the weight of ore need be accurate only to the nearest milligramme.[1]

[1] The easiest method for weighing out the proper quantity is to balance two pieces of smooth paper, which can be conveniently made of the same approximate weight by folding carefully a small sheet of writing paper and tearing it in two. A perfect balance can be made by tearing small pieces from the heavier half or by adjusting the rider. Instead of paper, balanced watch-glasses may be used. On the one scale place the required weight and on the other the ore. By using a small spatula ore may be removed or put on in small quantities, and the weight adjusted to within a milligramme, in a minute or two. Put the duplicate samples into small beakers with cover glasses. Add the hydrochloric acid slowly to one, taking care that there is no loss by effervescence, then add it to the other in the same way. By this time the first will be ready for the nitric acid, which must also be added slowly to it and afterwards to the duplicate. Then add the sulphuric acid just as carefully to the beakers in the same order. Hydrochloric acid being added first may get rid of some of the sulphur as sulphuretted hydrogen; nitric acid is liable to separate sulphur in the free state, which may liquefy and enclose some of the copper ore.

After the three acids have been added, heat on the hot plate till the hydrochloric and nitric acid are driven off, for otherwise the mixture would act on the platinum electrodes later. The presence of white fumes of sulphur trioxide ensure that the other acids have been driven off, therefore heat till copious white fumes appear, cool, add *cold* water slowly, and stir so that copper and other soluble sulphates may be dissolved. If water is added rapidly, insoluble basic salts may be formed. After about 50 c.c. of water has been added, heat and allow insoluble matter to settle, then filter and wash. The filtrate with washing should not amount to more than 100 c.c. Put into a tall 150-c.c. beaker.

(*b*) **Method of Electrolysis.**—The solution may be electrolysed as it is, but the copper deposit is not so coherent or so bright as if nitric acid is present. But 6 c.c. of acid is enough, too much would prevent the deposition of copper upon the electrode; hence add 4 or 5 grammes of ammonium nitrate, which provides nitric acid without increasing the total acidity. In the electrolysis of copper sulphate solution, copper is set free at the negative pole and the SO_4 radical at the positive acting on the water forms sulphuric acid and sets free oxygen. A possible decomposition of sulphuric acid at the same time would result in the setting free of hydrogen along with the copper, and this is said to be the cause of the incoherent deposition of copper. In the presence of nitric acid the hydrogen is oxidised, and the copper forms a bright deposit, other metals that are likely to be in the solution, such as iron, need a higher voltage than copper and are not deposited.

There are various forms of electrodes and correspondingly various modes of electric attachment, but we shall assume that the electrodes consist of a platinum spiral attached to the positive pole of a framework, and of a cylinder outside the spiral which can be attached by a shank of straight wire to the negative pole of the same framework. It is convenient to have a framework such that after the electrodes are put in place the beakers containing the copper solution can be raised on a stand or block so that the cylinder and the spiral within it will be covered with the liquid.

Clean the electrode from grease or any other dirt by dipping for a moment into a mixture of equal volumes of strong nitric acid and of water, which may be conveniently kept in a wide-mouthed bottle. Wash with tap water and attach to the framework, taking care not to touch the cylinder with the fingers or in any way by which the least dirt could get on it, otherwise the copper will not stick. A current of about $\frac{1}{4}$ ampere or less for a cathode area of 100 sq. cm. is about right, and 3 or 4 volts will give approximately that amount. The relation between voltage and amperage depends upon the electrical resistance of the liquid. A slight bubbling of gas from the positive pole indicates about the proper current. Often the current is passed during the night and by the next morning the copper should be all deposited. The liquid must

be tested to find out whether such is the case. Thoroughly stir the liquid by blowing through a glass tube, taking care not to jar the electrodes in such a way as to make them touch, because if they touch, a short circuit would be made which might cause a spark and would, at all events, allow the copper to be dissolved by the acid present. If the liquid were not stirred part of it might be free of copper and another part might still contain some. After the solution has been mixed take out a small quantity ($\frac{1}{2}$ c.c. or so) and put into a small porcelain dish or upon a test plate and add about an equal quantity of sulphuretted hydrogen water which may be prepared by passing the gas for half a minute or less through some water in a test tube. If there is blackening continue the electrolysis, if no blackening is produced the copper has been all deposited. In this case remove the block from beneath the beaker, but still hold the beaker in place with one hand and in the other hand take another beaker full of distilled water. Quickly lower the beaker which contained the copper and at once quickly replace it by the beaker of distilled water, taking care that the electrodes are not made to touch during the operation. The current between these electrodes, though still passing through the other solutions, is broken as soon as the beaker is removed, and if the thin film of acid were allowed to remain on the cylinder it would dissolve the coating of copper, so it is washed off immediately in the beaker full of distilled water. If there is another set of electrodes attached to the same framework treat them in the same way. When all the electrodes have been washed in the same manner, and not till then, turn off the current at the switch and remove the electrodes. After the current has been turned off there is, of course, no danger, even if the electrodes do touch, provided the copper coating is not actually scraped off. The cylinders which are now wet with distilled water might be dried by placing them on a hot plate, but they can be dried much more quickly if the water is washed off by a mixture of alcohol and ether. This mixture may be conveniently kept in a wide-mouthed bottle large enough to admit the cylinder. The alcohol and ether will evaporate in a minute or two with very little heat, as, for instance, on a steam plate. The electrode will cool in a minute or two and should then be weighed.

After weighing, dip into the nitric acid used for cleaning the electrode. The copper will instantly dissolve. Wash the cylinder with tap water, then with distilled water, dip into the alcohol and ether, and dry as before and weigh. The difference in the weight of the cylinder now and before is evidently the weight of the copper which was deposited on it. The results of duplicates should agree to within a few hundredths of a per cent. Two or three hours should be long enough for the actual work connected with the determination. If the filtering is not rapid, the duplicates can be filtered simultaneously. Filtration is, indeed, not really necessary, since the presence of an insoluble sediment does not affect the deposition of the copper. The time required for the plating out of the copper depends upon the current, and with the arrangement described rapid deposition is not feasible, because the deposit would not be coherent and could not be properly weighed. But if an electrode is rotated rapidly, a current of an ampere or more may be used, and the time correspondingly reduced. The effect of the rotating electrode is probably due, mainly, to the stirring by which copper is constantly brought to the cathode, where it can be deposited. Before testing the solution, to see if all the copper is removed, decrease the current to 0·1 ampere or thereabout, stop the rotating and proceed as before.

It has been assumed in the preceding directions that there is no silver in the ore. If there is any, it would be deposited with the copper, unless previously separated. A separation may be made by evaporating nearly to dryness, after the addition of hydrochloric acid and nitric acid, and before adding sulphuric, dissolving, as far as possible, in water, adding a drop or two of hydrochloric acid and filtering it. The filtrate should then be evaporated and sulphuric acid added, and the heating carried to white fumes. After taking up with water, if there is any precipitate of lead sulphate, it should be filtered off.

2. **CYANIDE METHOD.**—A method which may be used if the electric current is not available, or if a large number of determinations are to be made in a short time, is titration with potassium cyanide.[1]

[1] Titration methods are described in the next chapter, to which the student is referred.

This method depends upon the reduction of cupric salts to cuprous by the action of potassium cyanide in the presence of excess of ammonia. Cupric salts become a deep azure blue colour upon the addition of ammonia. The solution is decolorised by being changed into cuprous salt by the action of potassium cyanide. The copper being in the form of sulphate, the reaction may be represented by the equation

$$2Cu(NH_3)_4SO_4H_2O + 8KCN = K_4Cu_2(CN)_6 + NH_4CN \cdot NH_4CNO + 6NH_3 + 2K_2SO_4.$$

The main point about the equation is that it represents the change from cupric salt, $CuSO_4$, to cuprous, $K_4Cu_2(CN)_6$; the other parts of the equation might be called diagrammatic. It is not intended to state that potassium sulphate is formed, but no ammonium sulphate, or that ammonium cyanate is formed and no potassium cyanate. Indeed, the double cyanide of potassium and copper is given by some chemists as $K_2Cu_2(CN)_4$, and the following equation is copied from a German book of high standing:—

$$2Cu(NO_3)_2, 4NH_3 + 5KCN + H_2O = K_2Cu_2(CN)_4 + KCNO + 2KNO_3 + 2NH_4NO_3 + 6NH_3.$$

A great many things affect the reaction. Nickel, cobalt, zinc, silver, etc., which are acted on by potassium cyanide, must be absent. The quantity of ammonia, the temperature of titration, and the rate at which the potassium cyanide is added, have an influence. Metals that form insoluble hydroxides with ammonia are liable to retain copper and vitiate the results. The total volume of the solution also has an effect.

A solution of 22 grammes of cyanide per litre is a suitable strength. The solution must be standardised against pure copper or copper salt of known composition. The following method is recommended:—

Into a 200 c.c. beaker put about 0·150 gramme of copper, add about 10 c.c. of water and nitric acid, sufficient to start a fairly vigorous reaction, heat till the copper is dissolved, and boil till the gaseous oxides of nitrogen are driven off, dilute with cold water to about 75 c.c., add dilute caustic soda till a slight permanent precipitate is formed, add 6 c.c. of ammonia solution (specific gravity 0·90), then run in the cyanide solution

slowly and regularly till the colour becomes faint, dilute to 150 c.c., and continue adding cyanide, drop by drop, with constant stirring, till the colour is entirely discharged.

In determining the copper in an ore, make a sulphate solution, as before. Its volume after filtration should be about 75 c.c. Put in a couple of pieces of sheet aluminium, about $\frac{1}{16}$ inch thick, and between two and three square inches in area. Add a little more sulphuric acid, if necessary, and boil for about seven minutes. Some copper will be deposited on the aluminium, and some will probably form a loose metallic deposit in the beaker. Wash the aluminium foil with water, and in order to prevent the loose, finely divided copper re-dissolving, add to the liquid 15 c.c. or 20 c.c. of sulphuretted hydrogen water. Decant the liquid through a filter, wash the copper in the beaker by decantation, filter the washings, so as to retain any copper which might be poured from the beaker. Upon the aluminium sheet put about 5 c.c. of nitric acid (specific gravity, 1·2), and warm till the copper is dissolved. Pour the solution through the filter and catch it in the beaker containing the loose copper. Wash the aluminium sheet and the filter, and heat till all the copper is dissolved, and then proceed as in the standardising. If arsenic or antimony is deposited with the copper, it should be oxidised by adding three or four drops of bromine to the beaker and driving off the excess before the liquid is diluted with the washings. If these elements are not known to be absent, treatment with bromine is advisable, as a precautionary measure: carry out the titration as already described.

CHAPTER XI

ALKALIMETRY AND ACIDIMETRY

(TIME, SIX HOURS.)

1. **GENERAL CONSIDERATIONS.**—Alkalimetry and acidimetry illustrate the third general method of analysis given in the second chapter.

From the equation

$$NaOH + HCl = NaCl + H_2O$$

it is evident that 40 grammes of caustic soda neutralise 36·5 grammes of pure hydrochloric acid. This acid is not the ordinary strong hydrochloric acid of the laboratory, but the gas of which the latter is a solution. To neutralise 40 grammes of caustic soda nearly 100 grammes of what is usually called strong hydrochloric acid would be required. If 40 grammes of caustic soda and 36·5 grammes of hydrochloric acid are dissolved in separate quantities of water and each solution made up to a litre, the litre of sodium hydroxide solution would neutralise the litre of hydrochloric acid solution, and consequently any number of cubic centimetres of the sodium hydroxide solution would neutralise the same number of cubic centimetres of the acid. Of 36·5 grammes of hydrochloric acid 1 gramme is hydrogen.

The equation

$$2NaOH + H_2SO_4 = Na_2SO_4 + 2H_2O$$

shows that 80 grammes of sodium hydroxide is neutralised by 98 grammes of sulphuric acid, or 40 grammes of sodium hydroxide by the half of 98 grammes of sulphuric acid. Forty-nine grammes of sulphuric acid has the same neutralising value as 36·5 grammes of hydrochloric acid, and 49 grammes of sulphuric acid contains 1 gramme of hydrogen. If 49 grammes of sulphuric acid is made up to a litre with water, 1 c.c. of this solution will be equivalent in neutralising power to 1 c.c. of the hydrochloric acid solution. When a litre of solution

contains 1 gramme of replaceable hydrogen in the acid dissolved, the solution is called normal. A solution containing 36·5 grammes of hydrochloric acid or 49 grammes of sulphuric, or 63 grammes of nitric, or 91 grammes of hydrobromic, or 32·67 grammes of phosphoric is normal. But a litre of solution containing 40 grammes of caustic soda would exactly neutralise a litre of any of these acids, and such a solution is called normal. So also a solution containing 56 grammes of caustic potash in a litre is normal. A normal solution is usually defined as a solution containing one hydrogen gramme equivalent per litre. From the equation,

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O$$

it is evident that 106 grammes of sodium carbonate require twice 36·5 grammes of hydrochloric acid, and that therefore 53 grammes of sodium carbonate is equivalent to 36·5 grammes of hydrochloric acid, or that a solution, containing 53 grammes of sodium carbonate in a litre is normal. A solution containing half the hydrogen gramme equivalent per litre is half normal; a solution containing one-tenth of the hydrogen gramme equivalent is decinormal; a solution containing one-hundredth of the hydrogen gramme equivalent is centinormal.

Suppose a solution containing caustic soda or potash is found to require 20 c.c. of a normal solution of acid (hydrochloric or nitric or sulphuric, etc.) to neutralise it, the solution must contain the equivalent to 20 c.c. of a normal solution of caustic soda or of caustic potash, which an easy calculation gives as 0·8 gramme of soda, or 1·12 grammes of potash, since 20 c.c. is one-fiftieth part of a litre and in a normal solution contains one-fiftieth of the gramme equivalent, which in the case of caustic soda is 40 grammes, and of caustic potash is 56 grammes. In the same way the amount of hydrochloric acid or sulphuric or nitric in a solution could be determined if it were found that 43·67 c.c. of a half normal or tenth normal solution of potash or soda was necessary to neutralise it.

The general problem in alkalimetry and acidimetry is to make solutions of alkalies and of acids of the required strength and to use them in determining the quantity of acid or of alkali in an unknown substance.

2. **PREPARATION OF A STANDARD SOLUTION.**—A normal solution of caustic soda cannot be made by weighing out exactly 40 grammes and dissolving it in a litre. Caustic soda absorbs water so rapidly that the exact weight can hardly be obtained even if the substance were perfectly pure to start with, which is practically certain not to be the case, since sodium hydroxide absorbs carbon dioxide as well as water. Sodium carbonate, if specially prepared and dried, can be made sufficiently pure for use, and a normal solution can be made by dissolving 53 grammes of the carbonate in a litre.

Ordinary strong hydrochloric acid contains about 38 per cent. of the pure acid, but neither it nor the sulphuric acid nor nitric acid is sufficiently uniform in strength to be used for the purpose of making a standard solution, but though the strength of ordinary strong hydrochloric acid is not to be depended upon, the strength of hydrochloric acid of constant boiling point is nearly uniform. The best way in which to prepare this uniform solution is to make a solution of about 1·10 specific gravity by mixing the ordinary strong acid with an equal volume of water, putting a litre of the mixture into a large distilling flask and distilling till about three-fourths has passed over, then changing the receiver and collecting the next 150 to 200 c.c. separately. The specific gravity of this solution is 1·0962 at 25° C., and 180·170 grammes, or 164·42 c.c. at 25° C. in a litre gives a normal solution. This is accurate to one part in 10,000. Not so accurate a method, but probably well within 1 per cent. of error, is to evaporate about 600 c.c. from a litre of the acid made roughly to the specific gravity 1·10 and from the remainder to make a solution. The error would be inappreciable were it not for the impurities of the acid which are nearly all left in the residue, and for the fact that the temperature of the boiling liquid is not so likely to be the temperature of the vapour.

A normal solution is rather too concentrated for ordinary work and a half normal is more convenient. To make a half normal solution of hydrochloric acid weigh out on a rough balance into a dry, weighed beaker 90·085 grammes of acid prepared in either of the above ways, depending upon how accurate the results are required to be. The weight can be easily got within a centigramme by using a capillary pipette

joined to a piece of flexible rubber tubing. Pour the acid from the beaker into a litre measuring flask, rinse out the beaker several times with distilled water, pouring these rinsings into the flask, finally fill the flask up to the mark with distilled water, taking care that the water is of room temperature. If there are any drops of water in the flask above the mark remove them with a piece of filter paper, taking care not to soak up any of the acid. Stopper the flask and thoroughly mix the solution by alternately turning the flask upside down and right side up twenty times or oftener. Some chemists recommend pouring the solution out into a dry beaker and pouring backwards and forwards from beaker to flask several times. Too great care cannot be taken to mix the solution thoroughly.

When the solution has been made of the proper strength, it may, if desired, be removed to a glass-stoppered bottle. The best reagent for cleaning a bottle depends upon what has been in it before. Bottles that have been used for acid usually need nothing but water, bottles in which there is adherent matter can often be most readily cleaned with soap and distilled water and pieces of paper torn small enough to be got out again. The rubbing of the paper against the sides of the bottle when shaken is much more effective than one would naturally expect. When the bottle has been cleaned and thoroughly rinsed with distilled water, it should be drained as well as possible, then 10 to 15 c.c. of the solution should be poured in and shaken, so as to wash all the inside of the bottle, and then drained out. This operation should be repeated two or three times, otherwise the strength of the solution would be changed by being brought into the bottle.

3. **PROBLEMS.**—Various problems may be set in alkalimetry and acidimetry. The problems proposed for treatment here are, (*a*) to find the strength of a caustic soda solution in terms of half normal hydrochloric acid; (*b*) to make a solution of sulphuric acid equivalent to the hydrochloric acid; (*c*) to determine how far the work has been done accurately, by standardising the sulphuric acid against pure sodium carbonate; (*d*) to determine the alkali in soda ash, or of some mixture containing impure soda.

(*a*) A solution of caustic soda, slightly stronger than half normal, may be made by dissolving 22 or 23 grammes of sodium hydroxide in about 200 c.c. of water, cooling and diluting to a litre. It should be carefully borne in mind that all solutions should be of the laboratory temperature when made up to a definite volume, and hence, if heat or cold is developed during the dissolving process, the temperature should be properly adjusted before the final quantity of water is added, and the water should be of the laboratory temperature. Assuming that the hydrochloric acid solution is exact, the strength of the caustic soda may be determined. For this purpose use burettes, which must be perfectly clean, so that when the liquid is running out, drops will not be left on the side to produce an error in the reading. For cleansing burettes, a concentrated solution of potassium dichromate, to which strong sulphuric acid is added, is often recommended, but in most cases probably soap and distilled water is best. Use a brush like a test-tube brush, but with a long handle, or a long glass rod with a piece of rubber tubing on the end, for scrubbing out the burette. The water may be slightly warm,[1] but not hot, else it may change the volume of the burette and render the readings inaccurate. If a good cleaning with soap and water does not suffice, a warm concentrated solution of sulphuric acid and potassium dichromate may be tried. It will probably need to remain several hours in the burette.

Assuming that the burette is clean and has been washed out with distilled water, it will be necessary, before filling it for use, to rinse it out two or three times with about 10 c.c. of the solution, allowing it to run from end to end of the burette and draining it out carefully. When filling a burette, shake thoroughly the bottle containing the solution and pour directly from the bottle into the burette, best without using a funnel.

[1] Burettes differ slightly in the style of graduation, and some have special characteristics that affect the manner of reading. In the case of the more common ones there are longer lines (sometimes completely round the burette) at each cubic centimetre, and shorter lines at each tenth. In the case of transparent liquids it is easiest to read the level of the lowest part of the meniscus formed by the liquid, and the eye must be exactly on the same level as this part, or the reading will be inaccurate. The readings should be made to the second place of decimals. It is assumed that the burette used is fairly accurate. The calibration of burettes and pipettes is given in an appendix.

This precaution is to avoid any chance of change of concentration of the solution, due either to moisture in the dishes used or to evaporation. We shall assume that one burette is filled above the zero mark with acid and the other with caustic soda. Run out the liquid to the zero mark, taking care that no bubbles of air are left in the narrow tube below the stopcock. It is convenient, though not necessary, to start with both burettes at zero. Unless the liquid is run out very slowly, at least three minutes should elapse before the reading is taken, so that the liquid shall have all run down from the sides. This applies to all readings of burettes where accuracy is desired.

Put 50 to 100 c.c. of distilled water into a beaker and add a drop or two of methyl orange. Methyl orange is pink in the presence of strong acids, and pale yellow, or if very dilute, almost colourless in the presence of alkalies. It is possible that distilled water may contain a little ammonia, hence it is well to add a drop of acid from the burette and see if the liquid becomes pink. If it does not, add acid drop by drop, until the pink colour appears. The quantities of acid afterwards used must be measured from this point. If the pink colour appears with the first drop, run in about 10 c.c. of acid, and then, with stirring, run in the soda solution till the pink colour disappears, then add acid, drop by drop, till the pink colour returns. If the mark is overshot at any time, that is, if more acid or alkali is added than is required, it is easy to add some of the other solution. With care a point may be reached such that one drop of acid will turn the liquid pink and one of alkali will make it almost colourless. It is better to have only a drop or two of methyl orange in the liquid, because a change from pale pink to almost colourless is sharper than a change from a deeper pink through orange to yellow. The change is most easily seen by looking at the liquid obliquely. The liquid often looks colourless by light passing directly through it, while a distinct pink shade is seen if it is looked at obliquely. The eye soon gets tired if the liquid is looked at steadily, and the change of tint may not be visible, but after the eyes are rested by being turned away for a few moments the tint becomes quite marked when the liquid is again looked at. A little practice may be necessary before the beginner

can be quite sure of recognising the change of tint, but a few experiments will show him what degree of accuracy he has attained. It is best to take the readings always at the joint when the pink shade is just recognisable. This point varies with different people. Some people will detect the pink shade at a stage when others will require a drop or two more of acid to make the pink visible. Each one should titrate to the point at which he detects the first appearance of pink. Those whose eyes are not very sensitive may need to use a little more methyl orange than others, but each one should use the smallest possible amount of the indicator to which he is readily sensitive.

We shall assume that when the colour is just pink, the burette readings are: acid 10·45 c.c., and the alkali 9·87 c.c. Afterwards run out about as much more alkali and add acid till the same pink shade comes again. Repeat this operation several times. In this way, a series of numbers is obtained which may be put down in the record book in a manner similar to the following:—

Acid.					Alkali.
0·00	...	...	...	...	0·00
10·45	...	...	...	...	9·87
22·87	...	...	...	...	21·62
35·13	...	...	...	...	33·16
43·98	...	...	...	...	41·54
49·91	...	...	...	...	47·12 [1]

The value of the alkali in the terms of the acid can be obtained by dividing the figures in the first column by the corresponding figures in the second. The larger the numbers, the less will be the effect of an error in the reading, so that, other things being equal, the value got by dividing 49·91 by 47·12 ought to be the most accurate. The other numbers have a value in that they show whether the work has been done satisfactorily. The values obtained should in all cases be close. By making the calculation it will be found that

[1] The figures given here are on the assumption either that the water was perfectly neutral, or that the adjustment was made in the tint of the indicator before the burettes were run down to zero point. If the reading of the acid burette had been 0·27 c.c. and of the alkali 0·12 c.c., for instance, the other figures would have been correspondingly changed, and the figures given in the table would be got by the proper subtractions.

1 c.c. alkali = 1·0578 c.c. acid is the lowest value, and 1 c.c. alkali = 1·0595 c.c. acid is the highest value. The value obtained from the figures 49·91 and 47·12 is 1 c.c. alkali = 1·0592 c.c. acid.

Since the figures obtained in the several trials differ in the third place of decimals, it may be concluded that it is of no use to go beyond the third place of decimals, and 1 c.c. alkali = 1·059 c.c. acid may be taken as correct. On this assumption calculate the amount of acid that corresponds with the alkali in each case and see how far these differ from the figures given above, or still better, after having obtained your own figures, make the corresponding calculation.

(*b*) In order to make a sulphuric acid solution exactly equivalent to the hydrochloric acid it is advisable to first make a solution somewhat too strong, to find its strength and then dilute it appropriately. It is easier to add the proper amount of water to a too concentrated solution than to add acid to a too dilute one.

A half normal solution of sulphuric acid contains 24·5 grammes of H_2SO_4 to the litre. Ordinary strong sulphuric acid does not correspond exactly to the formula H_2SO_4, but contains a little water as well. Probably 26 grammes of this acid would be more than enough. Since the specific gravity is approximately 1·84 the volume would be somewhat less than 15 c.c. In order to be sure to have enough take 16 or 17 c.c. and dilute to a litre. Then standardise against the soda in the same way as was done with hydrochloric acid. Let us assume that as the result of the titration (as this operation is called) it is found that

1 c.c. sulphuric = 1·026 c.c. alkali.

The sulphuric acid is 1·026 times as strong as the alkali and, according to the figures above the alkali is 1·059 times as strong as the hydrochloric acid, and therefore the sulphuric acid is 1·026 × 1·059 = 1·086 times as strong as the hydrochloric acid, that is, 1,000 c.c. of this sulphuric acid would neutralise as much alkali as 1,086 c.c. of half normal hydrochloric acid would. It is evident that a litre of half normal sulphuric acid would contain only $\frac{1,000}{1,086}$ of a litre, or 920·8 c.c.

of the stronger acid. If less than 79 c.c. of the sulphuric acid has been used for the titration, pour out enough into a dry beaker to allow 79·2 c.c. of water to be added to the acid in the litre flask, and after the addition of this amount of water run out from a burette, pour acid back from the beaker till the liquid reaches the litre mark in the flask, and mix thoroughly. If too much acid has been used in the titration, it will be impossible to make a litre of sulphuric solution of the required strength, but ½ litre can be readily made. In order to test whether the solution is really equivalent, as it should be, to the hydrochloric acid it would be possible to titrate against the soda solution, and if 1 c.c. alkali = 1·059 c.c. sulphuric acid the result is exact; if it turns out that 1 c.c. alkali = 1·058 c.c. or 1·060 c.c. acid, the result is satisfactory, being within a reasonable limit of error.

(*c*) Instead of standardising the sulphuric acid against the caustic soda, and thus comparing with the half normal hydrochloric acid, it may be standardised against sodium carbonate. For this purpose, it is necessary to use the pure compound. Anhydrous sodium carbonate is a common reagent in the laboratory, and if manufactured by the ammonia soda process, is likely to be quite pure, but it should be tested for chloride and sulphate, and possibly for insoluble matter, and it is almost sure to contain some moisture. If no impurity except moisture is found, dry a quantity at a temperature between 150° C. and 200° C., allow to cool in a desiccator and transfer to a weighing bottle. Weigh out two lots of about a gramme each into beakers, dissolve in water and titrate with the sulphuric acid. One fourth of the formula weight, Na_2CO_3, or 26·5 grammes, should require 1,000 c.c., that is, 1 gramme should require 37·74 c.c. If this result, or within a tenth of a c.c. of it, is obtained, the work is satisfactory; if not, the error may be due either to incorrect diluting of the sulphuric acid or to the standard hydrochloric acid not being exact, or to inaccuracy of the measuring flask or burette. Assuming that the measuring vessels are accurate, the hydrochloric acid may be standardised against the sodium carbonate in the same manner that the sulphuric was, and this would determine whether the hydrochloric solution was made up correctly. The hydrochloric acid could also be tested by precipitating as

silver chloride and weighing. Since HCl corresponds to AgCl, a litre of normal acid would produce 143·38 grammes of silver chloride, hence, 20 c.c. of the half normal solution would produce 1·4338 grammes.

(*d*) To determine the alkaline content of soda ash or other material containing soda, weigh out 1 to 1·5 gramme of the substance, dissolve in water and titrate with a standard acid. If the acid is not exactly half normal, the proper calculation must be made. For instance, suppose 1·2560 grammes require 40 c.c. of acid which is ·5020 normal, calculate the percentage of alkali.

If the material were pure sodium carbonate, 1·2560 grammes would require 37·74 × 1·256 c.c. of half normal acid, and since the acid is stronger than the half normal solution, the quantity required will be less in the ratio 500/502, or 37·74 × 1·256 × 500/502 = 47·22 c.c. But according to the assumption the quantity required is 40 c.c., therefore the impure soda contains only 40/47·22 of pure carbonate or 84·72 per cent. In this calculation it is assumed that all of the alkali is in the form of sodium carbonate. If any of it were caustic soda, it would be calculated as though it were sodium carbonate. If a mixture contained 80 per cent. of sodium carbonate and 3·56 per cent. of caustic soda, it would be equivalent to 84·72 per cent. of sodium carbonate.

4. **REMARKS.**—The time required for this determination is given as six hours, but the student should endeavour to carry it out more rapidly. Half an hour is more than ample for making up the hydrochloric acid and soda solutions, provided the proper strength of hydrochloric acid is furnished by the laboratory and the flasks and bottles do not need cleaning. It is often convenient for two students to work together in preparing solutions and in cleaning the required vessels, and even in the titration. In no case, however, should one student make burette readings for both. Each should take his own reading and if, as sometimes happens, one may need a drop more acid than the other, in order that he may detect the pink colour, he should add it before taking the reading. A half hour's practice in testing one's ability to detect with accuracy the change of tint may be advisable before making the first set of comparisons between acid and alkali. Each of the sets of

titrations may require half an hour, but the student should aim at taking less time. The drying of the sodium carbonate should be going on while something else is being done, so that no time may be lost. The estimate of time on the basis above amounts to between three and four hours, and two hours, in addition, should be more than enough for calculations and time required for cleaning of dishes and similar operations. If, however, the student does not set out with the determination to lose no time, he will probably find at the end that he has consumed considerably more than the six hours allowed.

CHAPTER XII

CHLORIMETRY. BLEACHING POWDER

(TIME, FOUR HOURS.)

1. **GENERAL CONSIDERATIONS.**—When bleaching powder is acted upon by a strong acid, such as sulphuric or hydrochloric, chlorine is set free. This fact is made use of in the ordinary process of bleaching cotton. The chlorine thus obtained is called available chlorine, because it can be used for bleaching or other oxidising purposes.

The constitution of bleaching powder is not fully established, but it may be taken as $CaOCl_2$, and the action of sulphuric acid upon it as $CaOCl_2 + H_2SO_4 = CaSO_4 + H_2O + Cl_2$.

This equation represents the available chlorine as more than 50 per cent. of the bleaching powder, but the latter always contains moisture, at least, and bleaching powder containing 36 per cent. of chlorine is considered very good.

The value of bleaching powder is due to its available chlorine, and this is what is determined. The ordinary method seems, however, to be a determining of oxygen rather than of chlorine, but this amounts to the same thing, because the oxygen has its exact equivalent in chlorine. Suppose the chlorine to be taken away from $CaOCl_2$, there will be CaO left; if the oxygen is taken from $CaOCl_2$, there will be $CaCl_2$ left; and CaO and $CaCl_2$ are equivalent, and the two Cl's removed are equivalent to the one O removed.

Arsenious anhydride, As_2O_3, in taking up oxygen forms As_2O_5. This oxidation can be effected by bleaching powder and may be represented by the equation

$$As_2O_3 + 2CaOCl_2 = As_2O_5 + 2CaCl_2.$$

As_2O_3 needs 2O to oxidise it and 2O is equivalent to 4H, hence a normal solution of arsenious anhydride contains $\frac{As_2O_3}{4} =$ 49·5 grammes per litre, and a half litre will be more than

sufficient. Arsenious anhydride is very slightly soluble in water but can be dissolved in caustic soda or sodium carbonate or bicarbonate, the last being most suitable.

2. **PROCESS.** (*a*) **Preparation of Solutions.**—Into a beaker put 7 or 8 grammes of sodium bicarbonate and 2·475 grammes of arsenious anhydride, mix and add slowly with stirring, less than 100 c.c. of water and boil for a minute or two. If the arsenious anhydride does not all dissolve boil for a minute or two longer. If there is still a residue cool the liquid, decant the supernatant clear solution into a 500 c.c. measuring flask, add to the residue a little more sodium bicarbonate and about 50 c.c. of water and boil, cool the solution, bring it also into the measuring flask, rinse the beaker with water three or four times, bringing the rinsings into the flask, make up to the 500 c.c. mark, and thoroughly mix the liquid.

To prepare the bleaching powder weigh out 10 grammes in a watch-glass on a rough balancer (the fumes would attack a delicate balance) put into a porcelain mortar and rub with 50 to 75 c.c. of water. Allow to settle for a moment, pour off the turbid supernatant liquid into a litre flask, add more water to the mortar and repeat the operation till all of the bleaching powder is finely ground and is removed to the flask, then fill up with water to the mark. In order to get a uniform sample of solution and solid, it is necessary each time before removing any to vigorously shake the flask and thus thoroughly mix the material.

In titrating bleaching powder with the arsenic solution the best indicator is iodide starch paper. So long as any bleach remains in the solution a drop of it will colour the paper blue. When it has all been used up by the arsenic solution no blue colour will appear. The reaction is that iodine is set free from potassium iodide in a way that may be represented by the equation

$$CaOCl_2 + 2KI = CaO + 2KCl \times I_2,$$

though the action is not quite so simple.

The starch paper is made by dipping filter paper into a starch paste which contains potassium iodide, and then drying the paper. The best way to prepare starch paste is

to add to boiling water in a porcelain dish starch mixed with cold water to the consistency of a thin cream. Keep boiling while slowly adding the starch till a fairly thick paste is produced. Probably 1 gramme of starch to 200 c.c. of water will be about right. Add 2 grammes of potassium iodide dissolved in water. If the iodide is added to the water before the starch it is still more certain to be uniformly mixed.

(*b*) **Titration.**—As there is a litre of bleach and half a litre of arsenious solution a large number of determinations can be made, and it is convenient to make the first two or three very roughly and afterwards to be more accurate. Even from the first, however, the sample of bleach must be properly taken, or the later ones will be incorrect. Shake the flask vigorously, draw out 50 c.c. in a 50 c.c. pipette not taking much time because the solid particles settle rapidly. Put into a beaker, add 50 c.c. to 100 c.c. of water and then run in the arsenic solution from a burette, stirring the liquid all the time with a glass rod. Tear the starch paper into small pieces and touch one of these pieces with a drop of the liquid in the beaker after each 5 c.c. of arsenic solution is added until no blue colour is obtained. Suppose when 25 c.c. of arsenic solution had been run in the starch paper was turned blue by a drop of the liquid but that after 30 c.c. had been added there was no blue colour, it would follow that 50 c.c. of bleach could oxidise more than 25 c.c. and less than 30 c.c. of the arsenic solution. Fill up the burette again, take a fresh 50 c.c. of the bleach after carefully shaking the flask, add water as before and then arsenic solution. It is evident that 25 c.c. of the latter may be run in before testing with the starch paper, but after that, test on the addition of each cubic centimetre. Suppose that in this way it is found that the amount of arsenic solution required for 50 c.c. of bleach is between 28 and 29 c.c., take a third 50 c.c. of bleach and add 28 c.c. of arsenic solution and then test after each two or three drops. Suppose it is found in this way that 28·45 c.c. of arsenic solution is required; repeat the operation in exactly the same way for half-a-dozen times and if the figures obtained vary between 28·35 and 28·55 c.c. the result is fairly good. Two-tenths of a cubic centimetre between the highest and lowest figures is as much as should be allowed, and even this variation is rather large.

It is evident that the burette must be read to the second place of decimals.

3. **CALCULATION OF RESULTS.**—Let us assume that the average quantity of arsenic solution is 28·45 c.c. Since the solution is one-tenth normal it corresponds to a decinormal solution of chlorine which would have 3·55 grammes of chlorine for every litre, or ·00355 gramme of chlorine for every cubic centimetre, 28·45 c.c. of arsenic solution is, therefore, equivalent to 28·45 × ·00355 gramme of chlorine, and as this is the amount in 50 c.c. of the bleaching liquid, which contains ½ gramme of the bleaching powder, the amount of chlorine per gramme is 28·45 × ·00355 = 2 × ·2020 gramme or 20·20 per cent.

Caustic soda acts on iodine, discharging the colour because forming iodide and iodate

$$6NaOh + 3I_2 = 5NaI + NaIO_3 + 3H_2O,$$

hence, if the arsenious anhydride were dissolved in caustic soda it would tend to prevent the setting free of iodine when the bleach was placed on the starch paper. It is for this reason that sodium bicarbonate is in this case the most suitable solvent for arsenious anhydride.

4. **REMARKS.**—The time required for this determination is about three hours or less. Time is frequently lost in dissolving the arsenious anhydride; if too much water is added at first the operation may be slow. It is well to have made the starch paper during the attendance before the determination, as time is thus allowed for it to dry slowly, which is rather the better way. If the starch paper and the arsenic solution are prepared in the course of an hour at one attendance, the rest of the work should be done in an hour of the next attendance.

CHAPTER XIII

IRON ORE

(TIME, TEN HOURS.)

THE complete analysis of iron ore may involve many determinations, but we shall consider only the determination of insoluble matter, of iron and of total sulphur.

1. **INSOLUBLE MATTER.**—Some ores are readily decomposed by acids and do not need to be ground at all finely, but some, especially magnetites, are quite refractory, and require to be ground very finely, indeed, so finely that a small portion placed between the teeth does not feel gritty. These ores should be ground in an agate mortar, taking very small quantities at a time, about a twentieth of a gramme or less. It requires longer time to grind a given quantity to impalpable powder if taken in large quantities.

By insoluble matter is meant matter insoluble in hydrochloric and nitric acid; it consists mainly of silica and silicates.

The ore having been ground to the necessary fineness, weigh out a gramme or more (the quantity depending upon the probable percentage of insoluble matter) into a porcelain dish with a cover glass, and add 15 to 20 c.c. hydrochloric acid and a little nitric acid. Heat gently, till as much of the ore as possible is dissolved, and finally, heat to dryness at a temperature of 120° to 130° C. Add 5 to 10 c.c. of strong hydrochloric acid, allow to stand for a few minutes, then dilute with hot water, adding it slowly and stirring, to prevent the formation of insoluble basic salts. Dilute to about 100 c.c. and filter, washing with hot water containing a little hydrochloric acid, until the iron is completely removed, as shown by the washings, giving no red colour with potassium thiocyanate (sulphocyanide). The precipitate on the filter may be burned wet in a platinum crucible, and then heated on the blast for fifteen to twenty minutes. It is likely to have reached constant weight, and in commercial work it is not usual to heat a second time,

but one cannot be sure, without a second weighing, that the weight is really constant. The insoluble residue is, usually, largely silica, and is sometimes treated as being entirely so, but if one wishes to know the exact amount of silica, the residue must be subjected to further treatment.

One method is to add to the material in the crucible a few cubic centimetres of hydrofluoric acid and a drop or two of strong sulphuric acid. The free or combined silica is changed into silicon fluoride, SiF_4, which goes off as a gas, the bases are changed into sulphates. Iron or aluminium sulphate are further changed into oxide, Fe_2O_3 and Al_2O_3, sulphuric anhydride being given off. Hence, if the insoluble matter consisted of silica and silicates of iron and alumina, the weight of the residue subtracted from the weight of the original insoluble matter gives the amount of silica. If, however, there were calcium or magnesium silicates in the insoluble residue, sulphates of these metals would be left, and hence the amount of silica could not be obtained from subtracting the final weight from the original.

Another method for determining silica is to fuse the insoluble matter with six or eight times its weight of sodium carbonate, to remove the fused mass from the crucible with water and hydrochloric acid, to evaporate to dryness and heat to 120° to 130° C., afterwards moisten with strong hydrochloric acid, allow to stand a few minutes, dissolve in water, filter and wash with hot water, burn wet and ignite on the blast. The purity of the silica thus obtained may be tested with hydrofluoric and sulphuric acid, as described above. If the original insoluble matter contained barium sulphate, it would be left in the crucible after treatment with hydrofluoric acid.

2. **IRON.** (*a*) **General Considerations.**—The methods used commercially for determining iron are volumetric, and they depend upon the fact that iron has two oxides and salts corresponding to these oxides. Methods of this same kind cannot be used for such metals as zinc and aluminium, which have only one basic oxide.

From the equation

$$2FeCl_2 + Cl_2 = 2FeCl_3$$

it is evident that a given quantity of chlorine would change a

certain definite amount of ferrous chloride, $FeCl_2$, into ferric chloride, $FeCl_3$, and, of course, if the amount of ferrous chloride in a given solution were known, the amount of iron could easily be calculated. Similarly, if chlorine could be taken from ferric chloride forming ferrous chloride, the quantity of iron could be determined.

Chlorine dissolves in water, forming what is called chlorine water, but even if chlorine water were made of appropriate concentration, it would be impossible to keep the solution unchanged. On the other hand, chlorine may be taken from ferric chloride by stannous chloride, as shown by the equation

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4,$$

but a standard stannous chloride solution cannot be conveniently made or kept.

(*b*) **Preparation and Titration of Potassium Permanganate Solution.**—Potassium permanganate solution may be used to change the ferrous salt to ferric. When concentrated hydrochloric acid acts on solid potassium permanganate, chlorine is set free, according to the equation

$$2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2.$$

If the substances are in a very dilute solution, chlorine is set free to only a very slight extent, but in the presence of something which is easily oxidised, such as ferrous chloride, the action goes similarly to the following equation:—

$$KMnO_4 + 5FeCl_2 + 8HCl = KCl + MnCl_2 + 5FeCl_3 + 4H_2O.$$

From this equation it is evident that the weight of permanganate, represented by the formula $KMnO_4$, can produce the weight of chlorine represented by 5Cl or can change the weight of iron represented by 5Fe from the ferrous to the ferric condition. It follows that the normal solution of potassium permanganate contains $\frac{KMnO_4}{5} = 31{\cdot}6$ grammes per litre. This is far too concentrated, a decinormal solution 3·16 grammes per litre is more nearly suitable. Each cubic centimetre of this solution would oxidise ·00560 gramme of iron from the ferrous to the ferric condition. Some chemists prefer to use a solution such that 1 c.c. = 0·01 gramme of iron. In this

case if a gramme of iron ore be taken for analysis the number of cubic centimetres of permanganate required will give the percentage of iron and the solution may be called a percentage solution.

Potassium permanganate is not perfectly pure, and any organic dust or bits of cork would tend to decompose the solution. Hence it is well to take a little more than the theoretical amount required. For instance, if a percentage solution is required, dissolve about 5·75 grammes in about 500 c.c. of warm water, allow to stand for several hours and filter into a litre flask through glass wool or ignited asbestos (but not through paper which would act on the permanganate). Wash the residue, which is mainly hydrated manganese dioxide, due to reduction of the permanganate, fill the flask up to the mark and mix thoroughly.[1]

The fact that potassium permanganate is not usually pure involves that the strength of the solution must be determined in some way. A number of different methods are employed; the most common, though perhaps not the most accurate, is titration against ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4, 6H_2O$, often called Mohr's salt. It will be seen that if the salt either loses or absorbs water, or if the ferrous salt becomes oxidised by the air, an error is introduced. If clear crystals are chosen the error is small. By substituting the atomic weights it will be found that one-seventh of the Mohr's salt is iron; 3·5 grammes will therefore contain ½ gramme of iron, since it is convenient to complete a titration without needing to refill the burette, and since 50 c.c. burettes are ordinarily used, the amount of Mohr's salt to be taken for standardising depends upon the approximate strength of the permanganate employed. Usually the most suitable quantity is between 1·5 grammes and 3·5 grammes.

Weigh out a suitable quantity into a beaker, add 10 c.c. of strong sulphuric acid and then about 50 c.c. of water, cool and add to about 600 c.c. of water in a large porcelain dish or large beaker and titrate by adding potassium permanganate

[1] If potassium permanganate is obtained pure, a solution made with water obtained by boiling a dilute solution of chromic acid for several hours with a reflex condenser and then distilling in such a way that no organic matter can enter the permanganate solution will keep for years practically unchanged.

from a burette. If a beaker is used a piece of white paper should be placed beneath it.

The action of permanganate on ferrous sulphate in the presence of sulphuric acid is similar to that of permanganate on ferrous chloride in the presence of hydrochloric acid, and an equation should be made by the student to represent the reaction. The ammonium sulphate takes no part in the reaction; the double salt is used instead of ferrous sulphate because less liable to change. When all of the ferrous salt has been changed to ferric in the titration the addition of a single drop of permanganate gives a pink colour, which shows that the operation is complete. The permanganate is added rapidly at first, the liquid being stirred. When nearly all of the ferrous salt is oxidised the colour of the permanganate disappears more slowly than at first, and the reagent should be added drop by drop with careful stirring. The reading of the burette is taken when a colour is given to the liquid which remains after thorough stirring.

Suppose for 3·5 grammes of Mohr's salt 49·45 c.c. of permanganate is required:—

$$1 \text{ c.c. permanganate} = \frac{5}{49{\cdot}45} = {\cdot}01011 \text{ gramme iron.}$$

For the duplicate it is well to take a different amount. Suppose the quantity of permanganate required for 2 grammes of Mohr's salt is 28·35 c.c., it will be found by calculation that 1 c.c. permanganate = ·01007 gramme iron, which is sufficiently close.

(*c*) **Determination of Iron in the Ore.**—The ore is got into solution by treatment with hydrochloric acid. To ½ gramme or 1 gramme of ore in a small beaker add about 20 c.c. of strong hydrochloric acid, cover with a watch glass and heat nearly to boiling. The addition of stannous chloride helps the reaction, because as a reducing agent it acts on the iron of the ore. The quantity of stannous chloride to be added depends upon the quantity of iron in the ore; it is better not to add enough to make the solution quite colourless.[1] The solution of the ore should be evaporated till there is not more

[1] Stannous chloride may be conveniently made when wanted by heating a few pieces of tin with a little strong hydrochloric acid,

than 5 c.c. If the ore is apparently not entirely decomposed add acid and evaporate again. Add about 30 c.c. of boiling water and if the insoluble residue is white and evidently contains no iron it will not need to be filtered. A yellow colour in the solution shows that it contains ferric salt which must be reduced to ferrous before adding the permanganate.

To the boiling solution add dilute stannous chloride drop by drop from a pipette, stirring continually till the yellow colour disappears. If the solution of ore was colourless too much stannous chloride was added when dissolving it, and this stannous chloride must be oxidised in some way, conveniently by potassium permanganate or hydrogen peroxide added to the hot solution. Add one of these reagents till a slight yellow tint appears and then add stannous chloride to discharge the colour. The less the excess of stannous chloride the better. The reasons that the solution of the iron salt should be boiling are that the reduction of ferric chloride by stannous chloride takes place more quickly in the heat, and the yellow colour of the ferric chloride is much more distinct in hot solution and so the change to colourless is sharper. The slight excess of stannous chloride is best counteracted by adding mercuric chloride, since the white precipitate of mercurous chloride thus formed is not acted on by permanganate. The reaction is

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$

not only would a large quantity of stannous chloride produce an inconveniently big precipitate but there is danger that it will become black owing to reduction of the mercury salt to metallic mercury, as shown by the equation

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg.$$

In view of the way in which the reaction works, cool the iron solution after it is rendered colourless by stannous chloride and add 10 c.c. of a saturated solution of mercuric chloride.

It was stated above that in dilute solution potassium permanganate is little affected by hydrochloric acid, but there is a little action by which the permanganate is used up, thus indicating a higher percentage of iron than there really is. The quantity of strong acid should not be much more than

5 c.c., in which case its effect can be almost entirely counteracted by adding "preventive" solution. The preventive solution is made by dissolving 80 grammes of manganese sulphate in 875 c.c. of water, adding 165 c.c. of syrupy phosphoric acid (specific gravity 1·7) and 160 of strong sulphuric acid (specific gravity 1·84). Its action is said to be due to the manganese salt being oxidised by the chlorine and again reduced by the ferrous salt, so that in this roundabout way all of the permanganate used oxidises the iron. The phosphoric and sulphuric acids give a sharpness to the end point, because ferric phosphate and sulphate are not so strongly coloured as ferric chloride and the pink of the permanganate shows more readily. It is not allowable to add the preventive solution to the small beaker, because it acts on the mercurous chloride, forming mercurous sulphate, which is liable to decompose into mercuric sulphate and mercury. Hence in carrying out the operation add 10 c.c. of the preventive solution to 600 c.c. of water, and then add the contents of the small beaker containing the iron to it and titrate with permanganate, as when standardising against Mohr's salt. The process should be carried out as quickly as possible after the stannous chloride has been added, because ferrous salt is liable to be oxidised by the air.

If the residue after treatment of the iron ore with hydrochloric acid still contains iron, it must be filtered off, and after ignition may be decomposed either by treatment with hydrofluoric acid and sulphuric acid or by fusion with sodium bicarbonate. If the latter way is chosen, fuse with about eight times its weight of sodium carbonate for half an hour, remove from the crucible, dissolve in water and hydrochloric acid, add ammonia to precipitate ferric hydroxide, filter, wash two or three times, dissolve the ferric hydroxide in hot dilute hydrochloric acid and either add to the main iron solution before reducing with stannous chloride or determine the amount of the contained iron separately. The reason for precipitating the iron as hydroxide and redissolving is to separate it from the alkaline salt, because mercuric chloride forms double salts with alkaline chlorides which are easily reduced to metallic mercury, and so a black precipitate would be obtained instead of a white one, and the colour of the

permanganate would be obscured. Moreover, a small quantity of platinum may be obtained from the crucible. When stannous chloride is added, platinous chloride is formed, and this has a deep yellow colour, which appears as that of the iron disappears, and the reduction of the ferric salt to ferrous is not visible. When ferric hydroxide is precipitated from the solution by ammonia, the platinum goes into this filtrate and is thus separated from the iron.

3. **SULPHUR.**—The sulphur in an iron ore may be due to the presence of pyrites or other sulphur compound in the iron itself, or to some sulphate like gypsum or barite in the gangue. The sulphur needs to be oxidised in some way so that it can be determined as barium sulphate. One of the easiest methods is to fuse with sodium peroxide. Since platinum is strongly attacked by the fused peroxide, a crucible of less valuable material is used.[1]

A comparatively low temperature is required, a low red heat being quite sufficient; no higher temperature than is required to fuse the mass should be used. The quantity of ore to be taken depends upon its sulphur content; if the ore contains 5 per cent. or less 1 gramme is a reasonable amount.

Into a nickel crucible put 4 or 5 grammes of sodium peroxide mixed with about ½ gramme of sodium carbonate; upon that put 1 gramme of the ore and on top of that some more sodium peroxide, making about 6 grammes of peroxide in all. Fuse till the mass becomes quiet; about five minutes will probably be enough. Cool and put into cold water, taking care that the effervescence due to escape of oxygen caused by the action of sodium peroxide on water does not carry away any of the liquid. There must be enough water to prevent the liquid attacking the filter. After the disintegration is complete remove the crucible, carefully washing it; heat the liquid, allow the precipitate to settle, decant the supernatant liquid through a filter, add 50 c.c. or more of water to the residue and decant again, repeat this operation till the filtrate is at least 300 c.c., then bring the precipitate upon the filter and wash with water. To the filtrate add enough hydrochloric

[1] An iron crucible may be used provided the iron does not contain sulphur.

acid to acidify, heat to boiling and precipitate with barium chloride, using all the care that has been urged in the case of the sulphate in Chapter VI. The filtration and ignition are to be carried out in the manner there described.

It is well to consider what happens to the various constituents of the ore during the different processes to which it is subjected.

Besides iron and sulphur, common constituents are silica, alumina and calcium, and we shall assume the presence of barium and magnesium. Any of the common elements would act like some of these mentioned.

By the fusion sulphur is changed to sodium sulphate and the iron is oxidised. The exact condition in which all of the elements exist in the fused mass is not certainly known; they may form double silicates and aluminates, but on treatment with water sodium sulphate, silicate, and aluminate are soluble, the iron is precipitated as ferric hydroxide, and the barium, calcium, and magnesium are precipitated as carbonates. It was on account of these last that sodium carbonate was added to the peroxide. It will be noticed that ferric hydroxide and not ferric carbonate is precipitated. Ferric hydroxide is too weak a base to form a carbonate under these circumstances. Alumina, which acts in some cases as a base, acts in the presence of the alkalies as an acid forming a soluble aluminate and accompanying the sulphate and silicate. When acid is added to the filtrate the alumina is changed from an acid to a base, aluminium chloride being formed, and aluminium hydroxide could be precipitated from the solution by ammonia. Aluminium chloride is soluble, and is not affected by the subsequent addition of barium chloride.

The silicate, when in dilute solution, is not precipitated by the addition of dilute hydrochloric acid, though if it were evaporated to dryness, nearly all of the silica would become insoluble. On the addition of barium chloride, it and the sodium sulphate undergo double decomposition, barium sulphate being precipitated, while the other salts in solution undergo no change. There is a slight possibility that some silica may be mixed with the barium sulphate. This may be tested for by adding a little hydrofluoric acid and a few drops of sulphuric to the precipitate after it has been brought to

constant weight and seeing if there is any change in weight after evaporation and ignition.

It must be carefully noted that the fused mass is treated with water and not with acid. Acid is not added till after filtration, otherwise the iron and the carbonates would not be separated, and, worst of all, if barium were present, it would form a precipitate of barium sulphate in the wrong place.

The time required for the three determinations in iron ore is ten or twelve hours, but in order to do the work in this time, the three determinations should run concurrently; for instance, while the ore is being treated with acid for the insoluble matter and the iron, the fusion, etc., could be gone on with for the sulphur.

CHAPTER XIV

WATER

(TIME, FOUR HOURS.)

1. **HARDNESS.**—One of the most important things to be determined in water intended for engineering or industrial purposes is its hardness. Hard water, instead of readily giving a lather with soap, forms a curdy precipitate. Hardness is, ordinarily, due to the presence of lime or magnesia; the curdy precipitate produced by soap consists of calcium or magnesium salts of fatty acids, which in soap are combined with sodium.

Hard water, when evaporated, forms a deposit, the nature of which varies with the material, causing hardness. Calcium carbonate is practically insoluble in pure water, but is soluble in water containing carbon dioxide. When the latter is boiled off, the carbonate is deposited as a loose material, and the water becomes much softer. Hardness, due to calcium carbonate, is called temporary, because it can be largely got rid of by boiling. Calcium sulphate and magnesium salts produce a hardness that is not got rid of by boiling, and is therefore called permanent. The deposit in steam boilers caused by these salts forms a hard coherent scale.

Temporary hardness can be got rid of, not only by boiling, but also by the addition of slaked lime. Calcium carbonate dissolved in water containing carbon dioxide may be represented by the formula $CaH_2(CO_3)_2$, and the reaction with lime by the equation

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

The lime added and the lime originally dissolved in the water are precipitated as calcium carbonate. It is evident that the amount of lime to be added must be in proportion to the amount already in solution. This process for softening

water is called Clarking, from the name of the man who suggested it.

Clark's method for determining the hardness of water depends on determining how much soap solution of a given strength is required to use up the lime in solution in a given volume of water. The details are not given here, since the method, though in use for many years, is now being superseded.

(*a*) **Temporary Hardness.**—The newer method consists in determining the amount of lime present by titrating with acid.

As explained in the chapter on Alkalimetry and Acidimetry, a normal solution of hydrochloric acid contains 36·5 grammes of pure hydrochloric acid per litre.[1]

A normal solution is too concentrated for use in this case. a solution 1/50 normal is better. The equation

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

shows that two formula weights of acid are required for one formula weight of calcium carbonate, and so, if a normal solution of calcium carbonate could be made, it would contain 50 grammes (which is half the formula weight) per litre; a fiftieth normal solution would therefore contain 1 gramme per litre. For such solution, each cubic centimetre would require 1 c.c. of a fiftieth normal hydrochloric acid. Every cubic centimetre thus corresponds to 1 milligramme of calcium carbonate. Ordinary hard water contains much less than a gramme of calcium carbonate per litre, and in order to determine the amount of lime present as carbonate, take 100 c.c. of water and run in the acid till the calcium carbonate is all decomposed. This may be shown by using methyl orange as indicator in the water, to which the acid is added till the yellow colour changes to pink. A better indicator is alizarin. A drop of a mixture of 1 gramme of alizarin paste in 200 c.c. of water is enough. With alkalies, alizarin is violet, with acids, lemon yellow. Carbon dioxide has the effect of an acid upon alizarin, though not upon methyl orange, and on the addition of very little hydrochloric acid the violet colour changes to yellow. It is necessary, therefore, to boil the liquid and drive away the

[1] If the student has not done the work on alkalimetry and acidimetry, he should read what is said in Chapter X. about normal solutions.

carbon dioxide. The best method is to add more acid than is necessary (the approximate amount required could be found out by a rough experiment), to boil to drive off the carbon dioxide, and then to add fiftieth normal solution of caustic soda till the violet colour just appears. Boiling with acid in an ordinary glass is liable to dissolve some alkali, and thus vitiate the results, hence it is best to boil in a porcelain dish.

Suppose to 100 c.c. of water 20 c.c. of 1/50 normal acid is added, with alizarin indicator, and it is found that after boiling it is necessary to add 4·65 c.c. of 1/50 normal soda to give the violet colour, the amount of acid required for exact neutralisation is 15·35 c.c., which corresponds to 15·35 milligrammes of calcium carbonate, or, since 100 c.c. of water was used, to 15·35 parts in 100,000. Hardness is always reckoned in terms of calcium carbonate, even though it may be due to magnesia.

It is quite plain that the determination above does not give the hardness due to calcium sulphate or magnesium sulphate, because if the reaction

$$CaSO_4 + 2HCl = CaCl_2 + H_2SO_4$$

took place, a strong acid would be set free as soon as the first drop of hydrochloic acid was added, and the colour of the alizarin would be changed to yellow. It was, therefore, *temporary* hardness that was found in the above determination.

(*b*) **Permanent Hardness.**—In order to understand how the permanent hardness is determined, let us suppose that it is due to calcium sulphate. If sodium carbonate is added, an action represented by the equation

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

takes place. If there is just enough sodium carbonate for the calcium sulphate present, then after the double decomposition there would be sodium sulphate in solution and calcium carbonate precipitated, and if the calcium carbonate were filtered off, the filtrate would be perfectly neutral, because containing only sodium sulphate. Suppose 5 c.c. of 1/50 normal sodium carbonate had been added, it could give 5 milligrammes of calcium carbonate, so that the permanent hardness would be due to the calcium sulphate, which corresponds to the 5 milligrammes of calcium carbonate. If this was in 100 c.c. of

water, the permanent hardness would correspond to 5 parts of calcium carbonate per 100,000.

In actual work, a large excess of alkali is used, and since magnesia is more completely precipitated by sodium hydroxide than by sodium carbonate, a mixture of 20 c.c. of 1/50 normal sodium hydroxide and sodium carbonate is added to 200 c.c. of the water in a large porcelain dish, and the mixture boiled till the volume is less than 200 c.c. It is then cooled and brought into a 200 c.c. measuring flask, and the volume made up to the mark with distilled water. If there is time to allow the precipitate to settle, leaving the supernatant liquid clear, it is well to do so. Then draw off with a pipette, 100 c.c. of the clear liquid and titrate with 1/50 normal acid.

If there had been no permanent hardness, 20 c.c. of 1/50 normal acid would be required, because there is evidently half of the alkali which was put in. Suppose 17·30 c.c. of acid are required, 2·70 c.c. must have been used up by the permanent hardness, which corresponds to 2·70 milligrammes of calcium carbonate, or 2·70 parts in 100,000.

If there is not time to wait for the precipitate to settle, the liquid may be run through a dry filter. The filtrate which passes through first will have some of the alkali removed from it by the filter paper, so it must not be used for titration. After about 50 c.c. has passed through, collect the next 100 c.c. and titrate it.

Though 1/50 normal solutions are, usually, most convenient, if the water is very hard, 1/10 normal will be found better.

2. **CHLORINE.**—It is not the intention to describe the ordinary sanitary analysis of water, but one easily applied test will be given. All sewage contains chlorine, and though chlorine in water may come from an entirely harmless source, for instance, from salt deposits in the district, yet more than a few parts per million of chlorine is to be considered suspicious.

Water to be tested for chlorine should be neutral to litmus; the presence of carbon dioxide, which acts as acid to some indicators, does not hurt. If the water is acid, it should be neutralised with sodium carbonate; if alkaline, it may be

made slightly acid with nitric acid, and then made neutral with sodium carbonate.

Chlorine is most easily determined by the addition of silver nitrate. The precipitate formed is very small, and is not determined by weighing, but by measuring the quantity of silver nitrate solution necessary to exactly use up the chlorine present. The solution of silver nitrate most suitable is one in which 1 c.c. = ·001 gramme of chlorine. From the equation

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

it is seen that 170 grammes of silver nitrate are required for 35·5 grammes of chlorine, and so 4·79 grammes of silver nitrate per litre is the proper strength. The point at which sufficient silver nitrate has been added to the water is shown by using potassium chromate as indicator. Silver nitrate gives a red precipitate with potassium chromate, but will not do so while a chloride is in solution, silver chloride being formed in preference to silver chromate. The method of procedure is as follows :—

To 100 c.c. of water in a glass cylinder (Nessler's tube), add 1 c.c. of a 1 per cent. solution of neutral potassium chromate, and run in silver nitrate from a small burette, so graduated that hundredths of a cubic centimetre can be easily read. At first, if there is chlorine in the water, the precipitate will be quite white, but as soon as the chlorine is used up, a reddish brown colour appears. The proper end point is best determined by using a comparison tube containing the same amount of water and chromate, into which silver nitrate is run till the silver chromate distinctly appears. Then run in a drop or so of very dilute sodium chloride to discharge the colour. A comparison tube is thus provided which will look just the same as the test at the stage when nearly enough silver nitrate has been added to the latter. When the titration is made, compare the colour in the two tubes, and when there is a change in the one in which the test is being made, the correct point has been reached.

In ordinary water the quantity of silver nitrate solution will be only a few tenths of a cubic centimetre. Suppose the reading is 0·45 c.c., the quantity of chlorine would be 0·45 milligramme, or 4·5 parts per million.

If Nessler's tubes are not at hand, the determination may be made in a porcelain dish, into which 100 c.c. of water is measured.

3. **TOTAL SOLIDS.**—It is sometimes of interest to determine the total solids in water.

Evaporate 100 c.c. of water in a weighed platinum dish on the water bath. If the platinum dish is small, part of the measured quantity of water may be added from time to time, as evaporation permits, till the whole is evaporated. Dry the outside of the dish with filter paper, put it into the desiccator to cool and then weigh. Heat for half an hour in an air bath at about 105° C., and if there has been much loss, heat to constant weight. Gradually heat to redness, noting the changes that take place. The smell, change of colour, scintillation, separation of more or less carbon and partial fusion, if any, should be noted, as these give some idea of the character of the material.

The determination of hardness and of chlorine may be made in two or three hours if the standard solutions are ready; the total solids take little more time than is required for the weighings.

CHAPTER XV

IRON AND STEEL

THE qualities of iron and steel are affected by small quantities of impurities; a very small fraction, a percentage of phosphorus, for instance, may make a steel unfit for the purpose for which it was intended. The presence of silicon and carbon in pig iron affects the fusibility. Hence, iron and steel have frequently to be tested. We shall consider the determination of silicon, sulphur, phosphorus, manganese and carbon.

1. **SILICON.** (TIME, THREE HOURS.)—The determination of silicon involves oxidising it, separating from the constituents soluble in acid, and burning off the carbon which, like it, is insoluble.

To 1 gramme of drillings or shavings of pig iron, which need not be weighed more closely than to a couple of milligrammes, in a covered casserole, add slowly and without heating 25 to 30 c.c. of silicon mixture.[1]

After the vigorous effervescence has ceased, heat the covered casserole over a naked flame, giving the casserole a gentle motion. If the boiling is kept continuous and not too violent, any considerable sputtering will be avoided. In a very few moments the nitric acid will be all driven off, and dense, white fumes of sulphuric anhydride will appear. The strong heating is necessary to make the silica insoluble. Cool the contents of the casserole, add about 20 c.c. of cold hydrochloric acid containing one part of strong acid to two parts of water, digest at about 50° C. for five minutes, after which, wash off the cover glass into the casserole, add 50 to 100 c.c. of hot water, and

[1] Silicon mixture may be made by adding 250 c.c. of strong sulphuric acid to 800 c.c. of water, and 250 c.c. of strong nitric acid to its own volume of water. Cool each solution and mix them. Strong sulphuric and nitric acid do not act on iron so readily as dilute, and the above degree of dilution is satisfactory.

boil and filter. Sometimes this filtration goes slowly, but if a 7 c.c. filter, which is folded, as described in the footnote on p. 25, filters rapidly with pure water, and if the precipitate of carbon and silica is allowed to settle, there should be no difficulty. If the solution runs slowly at the beginning, it is well to dilute it with hot water, as it is quicker to filter a large quantity going rapidly than a smaller quantity going slowly. Wash with hot water containing hydrochloric acid till the iron is washed out; as shown by testing, the washings with potassium or ammonium thiocyanate (sometimes called sulphocyanide; the formula is KCNS or NH_4CNS).

Burn the filter wet, and ignite with free access of air; the platinum crucible being placed upon its side. The graphite, which has been left with the silica, burns best if not heated too strongly at first; a moderate, red heat is best. The important thing is to give free access of air to the carbon, and it is often advisable, from time to time, to remove the flame for a minute or two. This allows the mass to absorb oxygen, which, on heating again, promotes combustion.

The residue should be white, or nearly so. It may be finally heated for a few minutes on the blast. After cooling and weighing, it must be again heated to constant weight. It is well to stir the residue then with a stout platinum wire, and see whether there is any unburned graphite underneath. If there is, heat the residue again.[1]

A reddish colour in the residue indicates that the iron was not all washed out. If the residue is heated with hydrofluoric acid and a drop of sulphuric, the silica is all driven off and ferric oxide is left behind. From the amount of silica, the silicon can be calculated.

Steel contains less silicon than pig iron does, and 5 grammes of it should be taken for an analysis. The quantity of reagents

[1] Though the method described above is most generally satisfactory, the process may be carried on more rapidly by heating on the blast in the following manner: Lay the crucible on its side, open. Direct the blast against the crucible near the bottom at right angles to its length, so that the gases from the flame will not be near the mouth of the crucible. Heat for a minute, remove the flame far enough in to allow the crucible to cool, but do not allow the blast to pass the mouth of the crucible, or it may blow away some of the silica. In about ten seconds heat the crucible for another minute, and repeat heating and cooling till the residue is white. This will probably take about twenty minutes.

will need to be greater than stated above, though probably not five times as great.

The time required for carrying out a duplicate analysis up to the point of igniting the filter should be little more than an hour, but to attain this result it will be necessary to carry on the two determinations concurrently; for example, put the silicon mixture on the first, and while it is effervescing, put the silicon mixture on the second, the first can then be heated, and while it is cooling, heat the second. This plan may be continued. Two filters should be prepared at the same time; if the first filtration goes rapidly, it may be all that can be attended to, but if at any stage it runs slowly, filtration of the second may be begun, and the two run concurrently. The ignitions can be carried on while some other work is being done if the method indicated in the text is employed.

2. **SULPHUR.** (TIME, SEVEN HOURS.)—(*a*) **Determination as Hydrogen Sulphide by Evolution.**—Sulphur exists in several different forms in steel and pig iron, the most important being that of sulphide, which is decomposable by acid, giving hydrogen sulphide in the well-known way by treatment with acid. The sulphuretted hydrogen set free is passed into a solution of cadmium chloride, and the sulphide formed is afterwards decomposed by the addition of acid in the presence of so much water that the sulphuretted hydrogen set free is all dissolved by the water, and then the sulphuretted hydrogen is oxidised by iodine, according to the equation

$$H_2S + I_2 = 2HI + S.$$

The process may be carried out as follows: Into a $\frac{1}{2}$-litre flask, fitted with funnel and delivery tubes in the ordinary way, put 5 grammes of steel or iron filings. Connect the delivery tube with a glass tube reaching to the bottom of a test tube about 25 + 2·5 cm., in which there is about 20 c.c. of cadium chloride solution, which contains 20 grammes of cadium chloride dissolved in 500 c.c. of water, and made up to a litre with strong ammonia. To the solution in the test tube add enough water to make the test tube about two-thirds full. Put 75 to 100 c.c. of hydrochloric acid (specific gravity, 1·2) into the flask, and apply gentle heat till the iron is dissolved; then boil till the

sulphuretted hydrogen is all driven out of the flask. Empty the test tube into a beaker, rinse out and make the solution up to about 400 c.c. Add about 25 c.c. of hydrochloric acid (specific gravity, 1·16), making sure that the cadium sulphide completely dissolves, then add starch solution and iodine solution from a burette, till the blue colour of the starch becomes permanent, which will take place when the sulphuretted hydrogen is all decomposed, as represented in the equation above.

The iodine solution may be made by dissolving 2 grammes of resublimed iodine in 5 grammes of potassium iodide, dissolved in 50 c.c. of water and afterwards making up to a litre. The solution is not stable, but will vary within a few days, and must be standarised against a steel or iron of known sulphur content, treated in the same way as the test.[1]

(*b*) **Determination as Sulphate.**—Another method of determining sulphur depends upon the principle of changing the sulphur to sulphate and precipitating with barium chloride in the usual manner. Any sulphur existing in iron in the form of organic sulphides, like methyl sulphide, $(CH_3)_2S$, is not obtained by either this or the evolution method, but such sulphur is usually small in quantity.

To 200 c.c. of water and 8 c.c. of bromine, which must contain no sulphur, add in small quantities at a time 5 grammes of iron drillings, keeping the liquid cool. After solution, which takes place rapidly, there will be only a small quantity of bromine left, the iron being changed to ferric bromide and sulphate, which dissolves. Boil to drive off this excess of bromine, filter and wash the residue. Add to it about 2 grammes of sodium carbonate and burn the filter in a platinum crucible. Since gas often contains sulphur, alcohol flame is recommended. Then add a few crystals of potassium nitrate and heat again. Dissolve the mass in water, filter, acidify the filtrate and precipitate by adding barium chloride. Determine the barium sulphate as usual.

Into 130 c.c. of ammonia (specific gravity, 0·96) in a 500-c.c. flask, pour the filtrate containing the ferric bromide and sul-

[1] It may be more convenient to make the iodine solution by dissolving 0·4 gramme of potassium permanganate in 400 c.c. of water and 5 c.c. of sulphuric acid, then adding slowly a solution of about 8 grammes of potassium iodide dissolved in 200 or 300 c.c. of water, and diluting to a litre.

phate. This gives a precipitate of ferric hydroxide, and the sulphur is in the form of soluble ammonium sulphate. Fill the flask up to the mark and mix thoroughly. Filter through a dry filter, and after about 50 c.c. has run through, collect the next 300 c.c. in a beaker. Evaporate to 100 c.c., taking care that no sulphur gets in, then add enough hydrochloric acid to make slightly acid (probably five or six drops will be enough), and precipitate with barium chloride as usual. This precipitate was obtained from three-fifths of the iron, the precipitate got from the residue was from the whole of the iron. If three-fifths of the weight got from the residue be calculated, and the figures thus obtained added to the amount of barium sulphate got from the filtrate, the total weight would be the amount that would be furnished if all the sulphur of 3 grammes had been changed to barium sulphate, and hence the percentage of sulphur in the iron can be calculated.

The time required is from two to seven hours, depending on the method employed.

3. **PHOSPHORUS.** (TIME, EIGHT HOURS.) — The first stage in determining the phosphorus in iron is to oxidise it to phosphoric acid. This may be done in various ways ; one is by treating with nitric acid and potassium permanganate. The phosphate radical is separated from the iron by precipitating it as ammonium phospho-molybdate, and the phosphorus is determined in the precipitate. Dissolve 1 gramme of steel or iron in a 500-c.c. Erlenmeyer flask in 75 c.c. of nitric acid (specific gravity, 1·13). Heat till brown fumes cease to be given off, and to the boiling solution add a solution of potassium permanganate till a slightly permanent precipitate of brown oxide of manganese is obtained. If the solution of permanganate is concentrated, add only a few drops at a time. The phosphorus is thus completely oxidised, but it is necessary to re-dissolve the precipitated manganese. This can be done by adding a reducing agent, such as sugar, which changes the higher oxide to the lower basic oxide soluble in nitric acid. Remove the flask from the heat, add a very little granulated sugar and boil. If the liquid does not become clear, add another small quantity of sugar and heat again. Repeat the operation until the liquid does become clear ; the total quantity

of sugar should not be more than 50 milligrammes and may be less. If more sugar is used than is necessary, the phosphomolybdate does not precipitate well.

Cool the solution a little, and add ammonia slowly till a decided permanent precipitate of ferric hydroxide is obtained. When adding ammonia, hold the flask at an angle of 45 degrees, so that none of the liquid may be lost by sputtering. Add enough nitric acid to redissolve the precipitate, heat the solution to 85° C., and add 50 c.c. of the molybdate solution, whose composition is given below. Stopper the flask, cover with a towel to keep from cooling, and shake vigorously for five minutes. Filter through a 7-cm. filter paper. It is not necessary to remove the precipitated phosphomolybdate from the flask, but it must be washed free from iron. Wash the precipitate in the flask and on the filter with 5 per cent. molybdic reagent solution, till the washings do not redden potassium thiocyanate. Dissolve the precipitate on the filter with 2 or 3 c.c. of strong ammonia, catching the filtrate in the flask containing the rest of the phosphomolybdate precipitate. Remove the flask and place a 100 to 150 c.c. beaker under the funnel. Wash out the flask with successive small quantities of hot water and pour through the filter, and finally wash the filter. With care, the amount of filtrate should not be more than 30 c.c. Neutralise with strong hydrochloric acid; if the yellow phosphomolybdate begins to form, add ammonia until it redissolves. Add, very slowly, to the cold liquid, 10 c.c. of magnesia mixture, stirring constantly, but without touching the side of the beaker. After the magnesia mixture has all been added, add about one quarter the volume of strong ammonia and stir vigorously. It is well to place the beaker in cold water and to stir occasionally for some time. At least four hours should elapse before filtration. Filter the magnesium ammonium phosphate, and proceed as directed in the determination of magnesium in Chapter VI. From the amount of magnesium pyrophosphate obtained after ignition, the percentage of phosphorus can be calculated

If a number of determinations of phosphorus are to be made, it is easier to dissolve the phosphomolybdate precipitate in a measured quantity of standard caustic soda solution, and to titrate the excess of soda with standard nitric acid. The best

strength of each is such that 1 c.c. = ·0002 gramme of phosphorus, which is about 1·5 times decinormal.

The principle underlying this method is that ammonium phosphomolybdate is dissolved by caustic soda, the following equation being given for the reaction:—

$$2(NH_4)_3 . 12MoO_3 . PO_4 + 46NaOH$$
$$= 2(NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 22H_2O.$$

It is evident that the phosphomolybdate must be free from acid, hence after the iron has been washed out with dilute molybdic reagent, the latter must be washed out. For this purpose, a 0·1 per cent. solution of potassium nitrate is recommended. A certain amount of phosphomolybdate requires a definite amount of caustic soda, and so the strength of the caustic soda is standardised by treating iron whose phosphorus content is known, in exactly the same way as the iron which is being tested. If 1 gramme of the standard iron takes 20 c.c. of caustic soda to dissolve the phosphomolybdate derived from it, and 1 gramme of the test iron requires 15 c.c., it is plain that the latter contains three-fourths the percentage of phosphorus that the standard does.

To prepare the molybdic reagent dissolve 100 grammes of ammonium molybdate in cold water (pure), add 100 c.c. of ammonia solution (specific gravity, 0·92), and dilute to a litre. When wanted for use add a measured quantity of this solution slowly and with cooling to an equal volume of nitric acid of 1·20 specific gravity. The ammoniacal solution keeps well, but no more should be mixed with nitric acid than is required at the time. If more than 1 gramme of iron or steel is used in the determination, there must be a correspondingly larger amount of molybdic reagent. The total quantity of phosphorus in the iron or steel used in the determination should not be more than ·005 gramme.

To prepare magnesia mixture dissolve 110 grammes of crystallised magnesium chloride ($MgCl_2 . 6H_2O$) in water, and filter. Dissolve 28 grammes of ammonium chloride in water, add a little bromine and a slight excess of ammonia. Add this solution to the solution of magnesium chloride and add enough ammonia to make the solution smell decidedly of ammonia; dilute to about 2 litres, transfer to a bottle, shake

vigorously from time to time, allow to stand for several days, and filter into a small bottle as required for use.

The time required for the phosphorus determination is six or seven hours if the gravimetric method is used. The other method requires four or five hours if two samples of the test and two samples of the standard are carried through.

4. **MANGANESE.** (TIME, TWO HOURS.)—(*a*) **General Considerations.**—A method commonly used for determining manganese in iron and steel depends upon changing it into the highly oxidised permanganic acid, $HMnO_4$, which has the violet colour so well known in potassium permanganate. But permanganates are such strong oxidising agents themselves as to be somewhat easily decomposed, and all oxidising agents cannot be used. The ones so far found most satisfactory are lead peroxide and ammonium persulphate. Not only must the proper reagents be used, but they must be used in a definite specified manner. The method is one of comparison with a standard steel (or iron), and the standard steel and the test steel should be treated in exactly the same way. The manganese and iron are first got into solution as nitrates with dilute nitric acid (strong acid decomposes permanganate and must therefore not be used). Manganese nitrate is a salt of manganese oxide, MnO; permanganic acid corresponds to the anhydride Mn_2O_7 ($2HMnO_4 = H_2O, Mn_2O_7$), and the oxidising action of lead peroxide may be represented by the equation

$$2MnO + 5PbO_2 = Mn_2O_7 + 5PbO.$$

Permanganic anhydride with the water present gives the violet coloured permanganic acid, and lead oxide dissolves in the nitric acid

(*b*) **Method in which Lead Peroxide is Used.**—Dissolve 0·1 gramme in a test tube 10 inches long and 1 inch wide in 30 c.c. of nitric acid of 1·13 specific gravity, heat gently over the Bunsen till the steel is dissolved and the vapours in the tube are no longer brown. Add 0·5 gramme of lead peroxide and boil for a minute and a half, then cool by dipping the test tube into cold water; keep in a dark place till the lead peroxide has completely settled, which will probably take nearly an hour. It is well to do two samples of the standard and two of the test.

When the lead peroxide has settled, pour the clear liquid from a standard and a test steel into comparison tubes. The quantity of liquid should be nearly 30 c.c., since very little should have volatilised during the operation. One form of the comparison tube is the Eggertz tube, a graduated cylinder a little more than a centimetre in diameter. All tubes in a set must, of course, be of the same diameter. We shall assume that in each case the liquid measures 28 c.c. If on looking transversely through the tubes the colour is found to be exactly the same, the percentage of manganese in the test is the same as in the standard. But suppose that in order to get the same shade the test must be diluted to 35 c.c., it is evident that the percentage is greater than in the standard in the ratio of 35·28. Similarly the ratio between the test and standard can be formed in any case, and from the known percentage in the standard the percentage in the test can be calculated.

(*c*) **Method in which Ammonium Persulphate is Used.**—Ammonium persulphate may be used as an oxidising agent instead of lead peroxide, but it needs the addition of silver nitrate as a catalytic agent. The silver nitrate solution should contain 0·02 gramme of the salt; if there is less the action will not be sufficiently rapid, if there is much more a precipitate of silver peroxide will form and obscure the colour. It is said too, that dry ammonium persulphate does not act, it should be moistened.

Dissolve 0·2 gramme of steel (or 0·1 gramme if the manganese exceeds ·75 per cent.) in 10 c.c. of nitric acid (1·20 specific gravity), using test tubes 8 inches long and 1 inch wide, and heating in a boiling water bath till the nitrous fumes are all driven out, then add 15 c.c. of silver nitrate solution (containing 1·33 grammes of nitrate per litre) and 1 gramme of moist ammonium persulphate. Heat in the water bath till the colour begins to appear and then for half a minute longer. Remove the tubes from the bath while the evolution of oxygen continues and place in cold water. When the solutions are cool compare them as usual. This method is rather easier than the one with lead peroxide.

In pig iron there would be an insoluble residue after treatment with nitric acid. This should be filtered off and washed

with the silver nitrate solution in order not to increase the volume more than usual. The rest of the process is the same as described above.

5. **CARBON.** (TIME, TWO HOURS.)—The method here described applies only to the combined carbon in steel and does not determine the graphite in pig iron. Like the method for manganese, it is based upon a comparison of colours, the test steel and the standard steel being subjected to the same treatment. The standard steel should be of the same kind as the test steel, made by the same process, and in the same physical condition.

Into a test tube 15 cm. long put 0·2 gramme of the standard steel and, slowly, the proper amount of nitric acid (1·20 specific gravity). The proper amount of acid depends upon the percentage of carbon, for less than 0·3 per cent. of carbon 3 c.c. of acid is best; for 0·3—0·5 per cent., 4 c.c.; for 0·5—0·8 per cent., 5 c.c., etc. Since with the test steel the percentage is not known, it is well to take several samples and to add different amounts of acid. At least two of the standards should be run through at the same time. As the acid is added to each tube place it in a water bath of cold water and cover it with a small glass funnel or a marble, and when all the tubes are in place heat the water bath, not too rapidly, to boiling, and boil till all the carbon is dissolved, occasionally shaking the tubes. Graphite carbon is not dissolved and so, as stated above, cannot be determined in this way. The solution usually takes from twenty to forty-five minutes. As soon as the steel in any tube is dissolved place the tube containing it in cold water. Remove the solutions to comparison tubes and make the comparison as in the titration of manganese. It may be convenient to use comparison tubes of small diameter, *e.g.*, 7 millimetres, and to make the solution of the standard steel up to the volume or double the volume represented by the percentage of carbon. The volume of the solution of a steel containing 0·5 per cent. of carbon being made up to 5 c.c., the volume of the solution of the test steel would give its percentage, for example, if the volume of the solution of the test steel giving the same colour as the standard were 6·54 c.c., the carbon would be ·654 per cent.

CHAPTER XVI

LEAD ORE

(TIME, SIX HOURS.)

1. **CHROMATE METHOD.** (*a*) **General Considerations.**—One of the most delicate methods for determining lead seems to be very indirect, but as some parts of the operation take only a short time, the process is not longer than other more direct methods. The process involves a number of chemical reactions which are of interest. The lead, after being brought into solution, is precipitated as chromate, but instead of being weighed as such the lead chromate is treated with hydrochloric acid and after the addition of potassium iodide the iodine set free is titrated with sodium thiosulphate. Lead chromate heated with strong hydrochloric acid gives chlorine, as represented by the equation

$$2PbCrO_4 + 16HCl = 2PbCl_2 + 2CrCl_3 + 8H_2O + 3Cl_2.$$

With sufficiently dilute acid, especially if cold, however, chlorine is not set free, but the solution formed virtually contains chromic acid, as represented by the equation

$$PbCrO_4 + 2HCl = PbCl_2 + H_2CrO_4,$$

which, along with potassium iodide, sets free iodine:—

$$2H_2CrO_4 + 12HCl + 6HI = 6KCl + 2CrCl_3 + 8H_2O + 3I_2.$$

Iodine acts on sodium thiosulphate:—

$$6Na_2S_2O_3 + 3I_2 = 6NaI + 3Na_2S_4O_6.$$

By tracing back the equations it will be seen that $6Na_2S_2O_3$ corresponds to $2PbCrO_4$, and therefore $3Na_2S_2O_3$ to Pb. Crystallised sodium thiosulphate has the formula $Na_2S_2O_3$, $5H_2O$, and a little calculation will show that each cubic centimetre of a solution containing 18 grammes per litre equals

·005 gramme of lead. This is a suitable strength. The purity of the reagent is not to be relied upon, and the solution should be standardised as described later.

(*b*) **Process.**—Galena is one of the most common lead ores and it is found most frequently with calcite. We shall assume that the ore is one of this nature and that it contains in addition, a small quantity of siliceous matter and of iron oxide. In carrying out the determination, attention must be paid to a number of details which appear small but which affect the result. Fortunately, there is no difficulty in fulfilling the conditions.

Since galena is very heavy and calcite comparatively light, great care must be taken with sampling. After quartering in the usual manner, the small portion intended for the duplicate must be finely ground and carefully mixed. It is better not to pour from a weighing bottle, but to spread upon paper and to take small portions from various parts of the lot to make up the sample for analysis.

Dissolve the ore in a 250-c.c. Erlenmeyer flask by slowly adding about 15 c.c. of hydrochloric acid and (after waiting till the sulphuretted hydrogen has been nearly all driven off) 5 c.c. of nitric acid. Half a gramme of ore is sufficient if it contains over 25 per cent. of lead, very poor ores may need as much as 5 grammes. It is best to add hydrochloric acid before nitric acid, because nitric acid tends to oxidise the lead sulphide to sulphate which is not so readily soluble as the chloride, or to oxidise sulphuretted hydrogen to sulphur, which is liable to form a globule and may enclose some of the lead. Evaporate the acids till the volume is about 8 c.c. After cooling a little, add slightly diluted ammonia till there is a small permanent precipitate of hydroxide which, in the presence of iron will be reddish brown. Dissolve the precipitate in acetic acid, adding enough to smell strongly. If the solution is not clear add solid ammonium acetate in small quantities at a time, and warm, but do not boil lest basic ferric acetate should be precipitated. If there was a large quantity of ore, water may need to be added, but, if possible, keep the volume of solution below 50 c.c. and do not add more than 3 grammes of ammonium acetate, because the precipitate of lead chromate to be afterwards thrown down separates out best when the

solution is not too dilute, and does not contain too much ammonium acetate. Siliceous matter will not dissolve, but its presence does not interfere with the later operations unless it is in a gelatinous condition. The object of the ammonium acetate is to dissolve lead sulphate that may be present or lead chloride. Since lead chloride is soluble in hot water, it is well to have the solution as hot as possible without running the risk of precipitating ferric acetate. Add to the warm solution 10 c.c. of a 10 per cent. solution of potassium chromate. This is far more than is theoretically necessary, but an excess is needed, because lead chromate is not totally insoluble in ammonium acetate or at all events does not rapidly separate out, if only the exact calculated quantity of potassium chromate is added. If the volume is not much more than 50 c.c., if too much ammonium acetate has not been added, and if there is sufficient excess of potassium chromate, lead chromate separates out in a form that can be readily filtered after four or five minutes shaking. It is best to keep the liquid warm, and the shaking does not need to be so constant as to prevent the precipitation of two or three lots at the same time.

After five minutes, filter through a fairly large filter paper, say 11 cm. in diameter, spreading the precipitate thinly over a good deal of the paper. A good qualitative filter will do. If the funnel is very good, one filtration at a time may be all that can be attended to, but usually time is gained by doing two concurrently, and two filters should be got ready. It is well to have a very thin film of vaseline under the lip of the flask to prevent the lead chromate running down the outside. Pour the liquid, and as much of the precipitate as possible, upon the filter, keep the filtrate to see if any more lead chromate will separate out later, wash the flask with hot water, adding a few drops of dilute acetic acid each time, till the soluble chromate is nearly all removed, then with hot water containing no acid, because lead chromate is slightly soluble in even 0·5 per cent. acetic acid unless some soluble chromate is present as well. Acetic acid is not necessary at all except in the presence of a good deal of iron or manganese. The lead chromate need not all be removed from the flask, but the soluble chromate must be entirely got rid of. Wash the filter

thoroughly with hot water, testing the washings with lead acetate and acetic acid, till no cloudiness of lead chromate appears. If all of the potassium chromate has been washed out, doubtless the iron will be also. Ferric salts left behind would, like the potassium chromate, oxidise the iodide at a later stage and make the results too high. The filtration and washings of two precipitates should not take more than twenty minutes and may take less.

Dissolve the precipitate on the filter with a mixture of 25 c.c. of hydrochloric acid and 75 c.c. of cold water. It will probably be best to alternately treat the precipitate with portions of this dilute acid and with pure cold water. It is not important that all of the lead chloride formed should go through the filter, because it is not lead which is to be titrated later. However, if all of the lead chloride is dissolved, one is more certain that the chromate has all been decomposed and that none is left on the filter. A few cubic centimetres of hot water may be used to dissolve the chloride, but not enough to appreciably raise the temperature of the liquid in the flask, lest the action of hydrochloric acid, even though dilute, might set free chlorine which would be lost. After the chromate has all been dissolved, if there is any of the mixture of acid and water still remaining, add it to the liquid in the flask and dilute to about 200 c.c. Take the reading of the burette containing thiosulphate, after which add to the flask 1 gramme of potassium iodide, shaking very gently, just enough to diffuse the colour of the iodine through the liquid, and immediately run in the thiosulphate solution, drop by drop, at the rate of about three drops a second, shaking enough to keep the liquid uniform in colour throughout. Continue this till the brown colour of the iodine is nearly gone; unless there is very little chromate the colour will be dark green. Then add starch solution, made as described in the chapter on chlorimetry, except that no potassium iodide is added. There will be a deep blue colour. Now add thiosulphate, a very few drops at a time, and shake vigorously after each addition. Finally, when the blue colour has nearly gone, add 10 c.c. of strong hydrochloric acid, heat the liquid to about 40° C. and then add thiosulphate, a drop at a time, shaking vigorously till the liquid becomes clear and of a bright green colour.

The reaction between chromic acid and hydrochloric acid, and potassium iodide is not instantaneous, but takes a little time, and in such cases the quantity of reacting substances in the volume affects the rate. The chromic acid will be more rapidly used up if there is a large quantity of hydrochloric acid and of potassium iodide. There is a limit, however, to the quantity of acid and of iodide that should be used. Too much acid at first may set free iodine so rapidly that some of it may escape, and this would be the more likely to happen if the solution were warm. More than a gramme of iodide is likely to form a precipitate of lead iodide, which somewhat obscures the reaction. When nearly all of the chromic acid is decomposed a larger quantity of acid may be safely used, and the temperature may be raised.

If too much thiosulphate is added, a few drops of potassium chromate of known strength may be run in till the blue colour returns and then a drop of thiosulphate to discharge the colour. A solution of chromate containing 4·7 grammes per litre is approximately equivalent to the thiosulphate solution containing 18 grammes a litre. Of course, the amount of chromate added must be subtracted from the reading of the thiosulphate burette.

Possibly the last traces of chromic acid may not be decomposed, even with the care recommended above, but the amount is very trifling, and the error will probably be about equal in the ore and in the standard. Except with very rich ores, duplicates should agree within a tenth of a per cent. and may agree within two or three hundredths.

The method is not satisfactory in the presence of silver, bismuth, antimony, gelatinous silica, or a very large quantity of iron, but it may be modified by adding sulphuric acid after decomposition of the ore with hydrochloric and nitric acid, evaporating till white fumes appear, cooling, adding cold water, dissolving the soluble sulphates, filtering the lead sulphate, and after washing dissolving the precipitate in ammonium acetate, adding potassium chromate and treating the precipitate thus formed in the manner already described.

(*c*) **Standardising the Thiosulphate Solution.**—To standardise the thiosulphate solution either dissolve two quantities of pure

lead, of about 0·2 gramme each, in nitric acid [1] and proceed as with the ore, or dissolve a gramme of lead, make up the solution to 250 c.c. and take two quantities of 50 c.c. each, for the duplicate determinations. If the thiosulphate solution was made approximately correct, the quantity required for titration will be in the neighbourhood of 40 c.c.

The time required for the determination is about four hours. If the lead for standardising be first weighed out and started dissolving, it should be ready to go on with by the time the duplicate samples of the ore have been set on the hot plate to evaporate with hydrochloric and nitric acid, and these should be ready when the first are finished.

2. **MOLYBDATE METHOD.**—Another method for determining lead in ore is not so new but is in very common use. It is based upon the fact that ammonium molybdate gives a precipitate with lead. After enough molybdate has been added to precipitate the lead, any excess will give a yellow colour with a freshly prepared solution of tannin.

Treat the ore in a beaker with nitric acid and a little hydrochloric, then after cooling, add about 10 c.c. of sulphuric acid 1 : 1 ; evaporate till the greater part of the sulphuric acid is volatilised. Cool, add cold water slowly with stirring, till the volume is about 100 c.c., boil to dissolve the soluble sulphates and then cool for an hour if possible, by setting the beaker in cold water in order to ensure the complete precipitation of the lead sulphate. Decant through a filter leaving as much as possible of the precipitate in the beaker. Wash the precipitate with cold water containing about 1 per cent. of sulphuric acid, then to the residue in the beaker add boiling ammonium acetate solution containing enough ammonia to neutralise the small amount of sulphuric acid adhering to the precipitate and pour the solution through the filter. Repeat the operation till all of the lead sulphate is dissolved. Instead of the filter being washed in the funnel it may be put into the beaker and treated with boiling ammonium acetate. If there is a large quantity

[1] The best way to dissolve in nitric acid is to put about 10 c.c. of water upon the lead in an Erlenmeyer flask and to add strong nitric acid slowly till action begins. Then, on heating, the action will probably be sufficiently vigorous, if not, more acid may be added.

of insoluble sulphates, such as those of calcium and barium, boiling for half an hour may be necessary. Filter, and if possible, keep the bulk of the filtrate and washings below 100 c.c. Heat to boiling and add ammonium molybdate from a burette till a drop of the liquid taken from the beaker gives a yellow colour on the test plate with a drop of freshly prepared tannin solution containing about 1 gramme in 300 c.c. If the solution has become cold it must be heated to boiling again and the molybdate added till the colour is again obtained on the test plate.

In commercial work it is common to put the filter paper with the material on it into the beaker with the residue and to treat with ammonium acetate as before, either leaving the paper to disintegrate into shreds, or before it is broken up, washing it off into the beaker and then titrating the turbid liquid with ammonium molybdate.

The ammonium molybdate solution is conveniently made so that 1 c.c. is equivalent to ·0005 gramme of lead, which requires about 4·75 grammes per litre. It is standardised against pure lead or pure lead sulphate.

Since the colour does not appear with tannin until several drops of molybdate in excess have been added, a correction must be made whose amount depends upon the volume of the solution. Hence it is advisable to titrate always under as nearly similar conditions as possible. Some chemists claim to be able to detect the end point within one, or at most two-tenths, of a cubic centimetre, usually a greater correction is necessary.

CHAPTER XVII

NICKEL AND COBALT ORE

NICKEL and cobalt ores usually contain metals such as copper and arsenic, which may be precipitated with sulphuretted hydrogen, and are best got rid of in this way.

1. **DETERMINATION OF NICKEL AND COBALT TOGETHER.** (TIME, SEVEN HOURS.)—Dissolve the ore in 2 to 3 c.c. hydrochloric and nitric acid, add sulphuric acid and evaporate to white fumes, cool, add 5 or 10 c.c. of strong hydrochloric acid and heat for a little, then dilute with about 30 c.c. of hot water and pass a current of sulphuretted hydrogen in the heat. If arsenic is present, there should be some precipitate within five minutes, in which case pass the gas till no more precipitate seems to be formed. Then dilute still further, so that sulphides insoluble in dilute, though soluble in concentrated acid, may be precipitated and continue to pass the gas. When the precipitation seems to be complete, filter and wash the precipitate with hot water containing some sulphuretted hydrogen. Evaporate the filtrate with washings to about 75 c.c., driving off the hydrogen sulphide, and afterwards oxidising the iron with a little hydrogen peroxide, add ammonia, which precipitates the iron as ferric hydroxide, and keeps the nickel and cobalt in solution. If the iron had not been oxidised, it would have been somewhat soluble, and would afterwards contaminate the nickel and cobalt. The ferric hydroxide might be filtered off, but the precipitate is liable to retain some of the nickel and cobalt, and it would be necessary to dissolve it and reprecipitate. It is certainly easier and, probably, at least, quite as accurate to proceed with the electrolysis of the nickel and cobalt without removing the ferric hydroxide. Nickel and cobalt cannot be plated out from an acid solution as copper can, because hydrogen is separated at the cathode, instead of the metal; and a solution

with a large amount of ammonia along with ammonium sulphate or ammonium chloride is most suitable. After the ferric hydroxide has been precipitated, add an excess of 30 c.c. or more of strong ammonia and several grammes of solid ammonium sulphate.

A higher voltage and a greater current is used than in the case of copper. For the ordinary size of electrodes, say about 80 sq. cm., begin with half an ampere, and increase to an ampere. If the electrolysis goes on over night, from one quarter to one half ampere may be used, and in the morning the current increased to an ampere for ten or fifteen minutes. With rotating anodes, three amperes is allowable. There should be no nitrates present, hence it is safer to oxidise the iron with hydrogen peroxide than with nitric acid.

As in the case of copper, test with sulphuretted hydrogen, to see whether the nickel and cobalt are plated out. Since iron gives a black precipitate, it will be necessary to filter a little of the liquid and to test the clear filtrate. When the electrolysis is complete, remove the electrodes in the manner described under Copper.

If the deposit consists of pure nickel, it may sometimes be so nearly the colour of platinum as to be barely distinguishable. It is sometimes difficult to dissolve. Warm nitric acid (specific gravity, 1·20), is probably the best solvent. Great care must be taken to dissolve the nickel before heating the electrode more than is just necessary to dry off the alcohol and ether, because after heating, it is almost impossible to dissolve the nickel. When cobalt is present, the metallic coating does not usually look so well, but is brown or black. The results are often high, owing to the cobalt being impure. The cobalt plating is more easily removed than the nickel.

The time required for this determination depends largely upon the time needed for precipitation of arsenic by sulphuretted hydrogen. Often the student finds that, after he thinks the arsenic is all precipitated and has filtered, the filtrate gives a second precipitate when more sulphuretted hydrogen is passed, rendering necessary another filtration. By following carefully the instructions given above, this danger will be lessened. Six or eight hours ought to be an outside allowance of time for the determination.

2. SEPARATING OF NICKEL AND COBALT.—The separation of cobalt and nickel here given depends upon the fact that, by the action of potassium nitrite, cobalt is oxidised, and forms tripotassium cobaltic nitrite, $K_3Co(NO_2)_6$, which is precipitated. Nickel does not form the corresponding compound.

Evaporate to about 1 or 2 c.c. the solution obtained by dissolving the deposit of nickel and cobalt in nitric acid, nearly neutralise with caustic potash solution, add 5 grammes or more of potassium nitrite, dissolved in a little water and slightly acidified with acetic acid, stir, add acetic acid till the liquid is decidedly acid, and allow to stand in a warm place for twenty-four hours. The total volume should not be more than 50 c.c. Filter and wash with a dilute solution of potassium nitrite and potassium acetate.

The cobalt in the precipitate can be determined, by dissolving it in hot dilute sulphuric acid, boiling, to drive off the nitrous fumes, adding 5 c.c. of acetic acid and then a large excess of ammonia, and if there was not much excess of sulphuric acid, some ammonium sulphate and plating out as before.

There is such a large amount of salts in the filtrate that if nickel is to be determined, it is best to separate it from these, which can be done as follows: Boil the solution with hydrochloric acid to drive off nitrous fumes, precipitate the nickel with caustic soda and bromine, filter the oxide, dissolve and plate as usual.

CHAPTER XVIII

ZINC ORE

(TIME, SIX HOURS.)

1. **GENERAL CONSIDERATIONS.**—One of the most common methods for determining zinc is by titrating with potassium ferrocyanide with which it gives a white precipitate. Many other metals give also precipitates with potassium ferrocyanide, among which the deep blue with ferric salts and the chocolate brown with copper salts are well known. The rather elaborate treatment of the ore is for the purpose of obtaining all the zinc in the solution to be titrated and to eliminate everything else that would give a precipitate with ferrocyanide. Some hydroxides such as iron are insoluble in ammonia, and ammonium salts and are precipitated by this reagent. Others, such as cadmium and copper, are soluble in ammonia but are precipitated by sulphuretted hydrogen.

2. **PROCESS.**—To 0·5 gramme or 1 gramme or more of ore, depending on whether it is rich or otherwise, in a 500-c.c. pear-shaped flask (Kjeldahl flask) add about 10 c.c. strong nitric acid. If there is a large quantity of ore, somewhat more nitric acid should be added. Hold the flask in an almost horizontal position by a clamp upon the neck, and heat over a naked flame, keeping the liquid in constant motion. After the liquid is about half gone add 5 grammes of potassium chlorate and from 5 to 10 c.c. more of nitric acid. In all parts of the operation be careful to keep the mouth of the flask turned from you. Heat the mass as before, and when the material begins to be pasty spread it over the sides of the flask and heat till all becomes perfectly dry but not fused. It is well to heat the neck of the flask to prevent any moisture condensing there. The whole operation so far should not take more than eight or ten minutes. The large amount of potassium chlorate serves as a diluent of the dry residue and ensures

the completeness of the subsequent extraction of zinc. Cool the flask, add 35 c.c. of an ammoniacal solution, which is made by dissolving 200 grammes of ammonium chloride in a mixture of 500 c.c. of strong ammonia (specific gravity, 0·90) and 750 c.c. of water. Boil the contents of the flask for a few minutes very gently to avoid much loss of ammonia, then add 10 c.c. of bromine water and boil for a few minutes longer. This treatment renders the ferric hydroxide granular and less liable to retain zinc. The precipitate may also contain lead and manganese; bromine water oxidises manganese to the higher oxide which is precipitated, though the lower hydroxide is soluble.

Filter through a 9-cm. qualitative filter paper into a 400 c.c. beaker. Wash out the flask once with hot water, and after this washing has been passed through the filter remove the beaker and replace it by another. Neutralise the filtered liquid by adding strong hydrochloric acid till litmus paper turns red and then add 10 c.c. in excess. Cover the beakers and boil to decompose the chlorate, boiling till there is no more chlorine given off. Meantime wash the precipitate in the flask and on the filter with hot solution containing 100 grammes of ammonium chloride and 50 c.c. of strong ammonia to the litre. Add the washings to the first filtrate, neutralise with ammonia and then add 3 c.c. of strong hydrochloric acid, dilute with water to about 200 c.c. and add 50 c.c. of strong sulphuretted hydrogen water. If there is much copper it will be necessary to add more acid and to pass the gas through the liquid. If there is not much precipitate the liquid can be titrated without filtration.

Titrate with a solution of potassium ferrocyanide containing 22 grammes to the litre. Heat the zinc solution nearly to boiling; pour out into another beaker about one-third of it, and to the remainder add the ferrocyanide solution testing every 3 c.c. by putting a drop of the liquid into a drop of 5 per cent. uranium nitrate solution on a porcelain test plate. By only occasionally removing a drop or two of the zinc solution very little of the metal is lost. As soon as the brown colour appears on the test plate add most of the rest of the solution to the main quantity, and unless the solution is nearly boiling, heat again, and now, having some idea of how much

ferrocyanide is required, test cautiously when that point is reached, till the mark is slightly overshot, then add the remainder and test frequently. Since the liquid by this time contains very little zinc, it is allowable to take a larger quantity, say ½ c.c., for the test. Towards the end test after the addition of every three or four drops of ferrocyanide. Keep these tests and a note of the corresponding burette readings and after the brown tinge is obtained wait a minute or two to see if it appears in any of the earlier ones; if so, take the burette reading that corresponds to the earliest. A little ferrocyanide in excess, usually about two drops, is required to obtain the brown colour and this amount should be deducted.

The solution of ferrocyanide was intended to be such that 1 c.c. = ·005 gramme of zinc or with ½ gramme of ore each cubic centimetre would correspond to 1 per cent. metal. The ferrocyanide solution may be standardised against pure zinc. For this purpose weigh out carefully about 0·2 gramme of zinc, dissolve in 10 c.c. strong hydrochloric acid in a 400 c.c. beaker. Dilute, neutralise with ammonia, add 3 c.c. of strong hydrochloric acid, dilute to 250 c.c. and titrate as in the case of the ore. As in the case of lead, it may be easier to dissolve 1 gramme of zinc, make up the solution to 250 c.c. and take duplicates of 50 c.c. for standardising. The amount of ammonium salts in the standard should be nearly the same as in the ore, and even when the approximate amount of ferrocyanide required is known it is well to follow the regular course, as the operation should take about the same time for standard and for ore.

This method applies to most zinc ores, though some are too refractory to be decomposed in the manner described. For such ores a more advanced book must be consulted. This process may not entirely get rid of cadmium which would, therefore, count as zinc and which should be specially tested for.

The time required for the duplicates of ore and standard is about five hours. The duplicates should be carried on concurrently; for example, while the first is cooling after treatment with chlorate and nitric acid, the second should be brought up to that stage and be left to cool while the first is being advanced another stage.

CHAPTER XIX

BRONZE

(TIME, TWENTY HOURS.)

THE analysis of this alloy, while not so difficult as of one containing arsenic and antimony, presents some interesting features. We shall assume in the first place that the alloy contains tin, lead, copper, and zinc in fair quantities, with, perhaps, a little iron; afterwards, we shall consider the variation in the process which is suitable for such bronze as the American or Canadian cent, or the English penny.

The alloy must, in the first place, be cleaned if it is not bright. The ordinary tarnish of a coin can be scoured off by emery or some similar polishing material, and then wiped with a soft cloth. If there is any grease on the alloy, as may happen in the case of drillings or shavings, it may be cleaned off with ether.

The treatment of the alloy depends upon the fact that nitric acid forms soluble nitrates with all the metals present, except tin, with which it forms the insoluble hydrated oxide.

1. **TIN.**—Upon about ½ gramme of the alloy in a covered porcelain dish pour about 20 c.c. of water and add, slowly, nitric acid, till the action seems to be sufficiently vigorous. Warm, still keeping the cover on, till the action is complete. If the cover glass is kept on a little longer, it will be washed by the steam condensing in drops and falling back into the dish, after which it should be removed and the liquid evaporated to dryness. Moisten the residue with 1 or 2 c.c. of nitric acid, allow to stand for a few minutes, then add 50 c.c. or so of boiling water, slowly, and with stirring, and allow to stand in the heat for a few minutes.

The precipitate, which is hydrated tin oxide, is difficult to filter, tending to run through the filter. This difficulty may be avoided by adding to the liquid in the porcelain dish about

a milligramme of albumin dissolved in 10 c.c. of cold water. The albumin coagulates and carries with it the tin oxide, which can then be readily filtered, especially after boiling. Dry the precipitate and ignite in a *porcelain* crucible, finally with the blast, to get rid of the last trace of water, and weigh as stannic oxide, SnO_2. Tin oxide is not readily reduced to the metallic state, and if the filter is burned with care in the wire, is not likely to be decomposed. In case of doubt, moisten the substance in the crucible with nitric acid, heat continuously, till the excess of acid is driven off, ignite and weigh, as directed above.

In order to ascertain whether copper has been carried down with the tin, fuse in the porcelain crucible with sodium carbonate and sulphur, and dissolve the product in water. The fusion should not be long continued, for the crucible is acted upon. Tin and sodium form a sulpho-stannate soluble in water, copper gives a black, insoluble sulphide. If any copper sulphide is present, filter it off, washing with sulphuretted hydrogen water, dry, allow to fall into a porcelain crucible, moisten with nitric acid, heat, to convert the nitrate into oxide and weigh. This weight must be deducted from the weight of the pure tin oxide, and it must be added to the weight of the copper precipitate obtained later.

2. **LEAD.**—From the filtrate containing lead, copper, zinc, and, possibly, iron, lead can next be most conveniently separated. Lead forms an insoluble sulphate, while the sulphates of the other metals are soluble. But in order to obtain all the lead as insoluble sulphate, special precautions must be taken. Lead sulphate is perceptibly soluble in nitric acid, hence nitric acid must be got rid of. It is slightly soluble in pure water, less soluble in water containing sulphuric acid or alcohol.

To the filtrate from the tin add 5 c.c. of strong sulphuric acid, evaporate to a very small bulk in a porcelain casserole, and then, after putting a cover glass upon it, heat, by giving the casserole a gentle and regular motion over a naked flame (Bunsen), till dense, white fumes of sulphuric anhydride are given off. Cool, and as usual, add cold water slowly and with stirring, to prevent formation of insoluble basic salts. After

about 75 c.c. of water has been added, boil, to make certain of the solution of copper and zinc sulphate, and allow to stand for an hour or so more in a warm place. Pour the clear liquid through a filter, wash by decantation, and afterwards, on the filter with water containing about 1 per cent. of sulphuric acid. The acid should be added to cold water, and the solution thus obtained should be heated. After the copper has all been washed out, as may be tested by adding ammonia to 3 c.c. of the washings, change the receiver and wash the filter with a mixture of equal volume of alcohol and water till the washings give no precipitate with barium chloride.[1]

These washings may be put into a bottle of alcohol residues; they contain no metal. The washing with alcohol and water is intended merely to get rid of sulphuric acid, which would char the paper on drying, and make the ignition troublesome.[2]

After the filter has been dried, remove the precipitate (if there is enough of it) to glazed paper, burn the filter in a wire, as carefully as in the case of silver chloride, allow the ash to fall into a porcelain crucible, moisten with nitric acid, to dissolve any lead that may have been reduced to the metallic state, and add a drop of sulphuric acid to change it to sulphate. Heat till the acid is driven off, add the main bulk of the precipitate and ignite at a low, red heat. Too high a temperature might decompose some of the sulphate. From the weight of sulphate the lead may be calculated.

3. **COPPER.**—The copper may be most easily separated from the filtrate from lead sulphate by electrolysis, but for the sake of practice another method should be adopted here. Copper is precipitated by sulphuretted hydrogen as cupric sulphide, CuS, in an acid solution, while zinc is not thrown down. Cupric sulphide is liable to be oxidised to sulphate which is soluble, and so the precipitate should be washed with water

[1] Since barium chloride is not readily soluble in water containing alcohol, be careful not to mistake a precipitate of barium chloride for barium sulphate. The former is dissolved by the addition of more water; the latter is not.

[2] It is stated by some chemists that lead sulphate is slightly soluble in even dilute sulphuric acid, and they advise washing the lead sulphate precipitate with combined alcohol and dilute sulphuric acid until all other salts are washed out and then washing with alcohol alone. In this case the alcoholic washings would be in the solution containing copper and zinc, and should be got rid of by evaporation.

containing sulphuretted hydrogen. The sulphide is apt to run through the filter, but if precipitated in the heat it is more dense, filters better, and is more easily washed than if the liquid is cold. To prevent spurting by the passage of the gas, and to limit access of air, an Erlenmeyer flask should be used, from which the precipitate may be readily washed out if the directions are carefully followed.

Put the filtrate from the lead and the washings with dilute sulphuric acid, which together should not be much more than 100 c.c. into a 250 c.c. Erlenmeyer flask and heat to boiling. Pass in sulphuretted hydrogen for five or ten minutes. Stop the current of gas, allow the precipitate to settle, which it should do in a minute or less, and see if there is any colour in the supernatant liquid. If there is, add more water and pass the gas again for a few minutes. It may be best to take this precaution in any case. Filter the precipitate as quickly as possible. It should be so loose as to be easily washed out. Unless one has a small funnel that runs specially well it is best to use a filter of 7 or possibly even of 9 c.c., folded as described in the footnote on p. 25. In washing out the flask put in hot water saturated with sulphuretted hydrogen. Use no more water than can be emptied at one time into the filter. If the filter is running at all properly the one lot of washing water should have run through by the time the next quantity is ready to be poured from the flask.

After the cupric sulphide has been dried remove it to glazed paper, burn the filter, moisten the ash with nitric acid in a porcelain crucible and heat to convert the cupric nitrate into cupric oxide. The best form of crucible is the Rose crucible, named after the distinguished chemist who introduced it into analytical work. Remove the cupric sulphide from the glazed paper to the crucible, mix the precipitate with some powdered sulphur, pass a stream of hydrogen through a porcelain tube that fits into a hole in the lid of the Rose crucible, and when the air has been entirely driven out heat the crucible first with a small flame and afterwards with the full flame of a Bunsen burner. The hydrogen should be passed though a wash bottle, and at first there should not be more than four bubbles a second, at the end there may be twice that number. Heat till the sulphur which has not combined with the copper is all

driven off. This can be seen by removing the cover for a moment and seeing that there is no blue flame or smell of burning sulphur. Allow the crucible to cool in a stream of hydrogen till there is no danger of the precipitate being affected by the air. Complete the cooling in a desiccator, and weigh as cuprous sulphide, Cu_2S.

It might naturally be thought unnecessary to add sulphur since cupric sulphide has more sulphur than cuprous sulphide, and the reaction goes according to the equation

$$2CuS = Cu_2S + S,$$

but there is danger of sulphur being volatilised before the change is complete. It is evident that the sulphur must be pure. This can be tested by making a blank experiment, and if a residue is left the sulphur should be purified by dissolving in carbon bisulphide and crystallising from the solution.

If a Rose crucible is not at hand, an ordinary crucible may be used, and the cover from time to time removed for a few seconds. In this way the cupric sulphide, CuS, is changed mainly to a mixture of cuprous sulphide, Cu_2S, and cupric oxide, CuO. Since the atomic weight of sulphur is just double that of oxygen, the proportion of copper in each of these is the same. This method is not quite so accurate as the former, probably because there is not the same certainty that all of the cupric sulphide has been changed.

Another method suggested for the determination of copper is to change the sulphide to sulphate and to weigh in that form. Dissolve the copper sulphide in nitric acid, add two or three drops of strong sulphuric acid, and evaporate at about 200° C. till the acid has all volatilised. If the copper sulphate is heated too strongly, it loses, at least, part of the sulphur trioxide, but not if the residue left after the volatilisation of the acid is cupric sulphate.

4. **ZINC.**—The filtrate from the copper sulphide must be heated to drive off sulphuretted hydrogen. It is well to have found out beforehand, by a qualitative analysis or otherwise, whether the alloy contains any iron, since if it does, ammonia must be added, whereas, if it does not, ammonia should be omitted. If iron is present, it must be oxidised, for which purpose a little nitric acid or hydrogen peroxide is suitable.

Then the iron is precipitated as ferric hydroxide, washing carefully, as described in Chapter VIII., igniting and weighing.

From the filtrate, ammonia must be driven off by heating with a slight excess of caustic soda in a platinum or porcelain dish. Zinc is kept in solution by ammonia or by soda, but when the ammonia is all driven off, the soda may be neutralised by the addition of sulphuric or hydrochloric acid, and the zinc precipitated as carbonate by sodium carbonate. For this purpose, to the cold zinc solution in a large porcelain dish, add sodium carbonate solution, drop by drop, till the zinc solution becomes turbid, then heat to boiling. In this way, the greater part of the zinc is precipitated as granular zinc carbonate. If the liquid is strongly alkaline, the precipitate is liable to be contaminated with the alkali; hence, in order to avoid adding too much sodium carbonate, put in a drop or two of phenolphthalein and add sodium carbonate till the pink colour becomes quite distinct, but no more. Allow the precipitate to settle, filter off the clear liquid, wash the precipitate several times with hot water by decantation, and then on the filter, till a couple of cubic centimetres gives no precipitate with barium chloride, and then wash a few times more. Dry the precipitate and remove from the filter to the glazed paper, burn the filter, either in the wire or in a porcelain crucible. It may be well to moisten the paper with a saturated solution of ammonium nitrate, in order to oxidise it and prevent the reduction of zinc oxide to metal, which would be lost by volatilisation. The ignition should be carried on at the lowest possible temperature. Moisten the ash in the crucible with a drop of nitric acid, heat to dryness, add the zinc carbonate on the glazed paper, and heat the crucible to change it to zinc oxide, heating gently at first, and afterwards with the highest temperature of the Bunsen, and even with the blast. The filtrate should be tested by passing sulphuretted hydrogen through it, best in a flask, which can be corked after the liquid has been saturated with the gas. There should be no more than a very slight precipitate, even after twenty-four hours.

The method just described is open to the objection that, in the presence of sulphates, zinc carbonate is likely to be contaminated with basic zinc sulphate, which should decompose into zinc oxide when strongly heated, but which may not be

completely changed. Some chemists prefer to precipitate zinc as zinc sulphide.

There are two difficulties in this determination, one that zinc sulphide is easily oxidised, another that it is difficult to filter, being liable to form a somewhat slimy precipitate, which clogs the filter but at the same time is liable to run through on washing. Zinc sulphide is readily soluble in mineral acids, but not in acetic acid. Colourless ammonium sulphide precipitates it slowly; it is slightly soluble in yellow ammonium sulphide. The presence of other ammonium salts seems to help in the precipitation.

In accordance with these facts, the following method is recommended: To the slightly acid solution in an Erlenmeyer flask, add sodium carbonate till a permanent precipitate is formed. Dissolve this with a little ammonia, just enough for the purpose, add 5 grammes of ammonium acetate or of ammonium thiocyanate for every 100 c.c. of solution, and a solution of a freshly prepared ammonium sulphide, somewhat in excess of what is required for precipitation, fill the flask with boiling water, so that no air may be left, either in the water or in the space above it, cork the flask and allow it to stand in a warm place for twenty-four hours. Without disturbing the precipitate, pour the clear supernatant liquid into another flask, cover the precipitate with 30 or 40 c.c. of a 5 per cent. solution of ammonium thiocyanate and a cubic centimetre of ammonium sulphide solution; allow to settle a minute or two, pour off the supernatant liquid into the flask as before and repeat this operation two or three times. Finally, leave the precipitate with the wash solution upon it and the flask corked, while the liquid, which has been decanted, is run through the filter, then, after changing the receiver, bring the main precipitate upon the filter, wash out the flask, wash the precipitate first with the wash mixture described above and, finally, with water containing only ammonium sulphide. The wash water in this case should not be allowed to run out each time, but should be poured in at the top as rapidly as it runs out, the filter being thus kept full. This takes a good deal of liquid, but it prevents exposure of the zinc sulphide to the air. After the washing is finished, dry the precipitate, remove it to the glazed paper, burn the filter, allow the ash to fall into a Rose

crucible, put in the main precipitate and about one-third its weight of sulphur, mix the two with a platinum wire and heat in a current of hydrogen, just as in the case of copper. The substance thus obtained is zinc sulphide, ZuS.

Another method of precipitating zinc sulphide is to add sodium carbonate till a permanent precipitate is obtained, to dissolve this with a drop of hydrochloric acid, pass sulphuretted hydrogen, till no more precipitate is formed, add several grammes of sodium acetate and pass sulphuretted hydrogen again.

The time required for the bronze analysis is about twenty hours.

APPENDICES

APPENDIX A

THE BALANCE AND WEIGHTS

THE essential features of the ordinary analytical balance are the beam supported at the middle on a knife-edge, and hanging from the ends of the beam two scale pans, in one of which is placed the object to be weighed and in the other the weights to counterpoise it. There are details in construction which affect the delicacy of the balance which need not be discussed here.

For accuracy the arms must, in general, be of equal length, the point of suspension should lie above the centre of gravity, and the knife-edge on which the beam is supported and those from which the pans are suspended should be in the same plane and parallel to one another. To test whether the arms are of equal length place the object on the left pan and counterpoise by weights on the right. Then place the object on the right pan and the weights on the left, and if the arms are equal the weights will be the same in both cases. When there is no weight on either pan the balance should swing nearly evenly, as shown by the pointer. If the deviation is too great, adjustment may be made by a nut on a screw thread at the end of the arms.

For sensitiveness, other things being equal, the longer the arms the more sensitive and the higher the centre of gravity the more sensitive. But if the arms are long and the centre of gravity high the time required for the swing is increased and the centre of gravity must not be above the axis of oscillation of the balance, otherwise there would be unstable equilibrium. By moving a nut up or down on a vertical screw thread, the centre of gravity may be raised or lowered. In ordinary cases the balance is not adjusted to its extreme sensitiveness, as this would make the oscillation too slow.

The weights should be tested for accuracy. Most sets of weights have three of 1 gramme each, one of 2 grammes, one of 5 grammes, two of 10 grammes, one of 20 grammes, and one of 50 grammes. Place one of the 1-gramme weights on

the right-hand pan and another on the left. We shall assume that they balance. Reverse the position and if they still balance you have proved that they are equal and that the arms of the beam are of the same length. Now balance the third 1-gramme weight against either of the other two. Then balance the 2-gramme weight against two of the 1-gramme weights, also the five against the two and the three ones. Balance each of the 10-gramme weights against the small ones whose sum is ten, then the twenty against the two tens and the fifty against all of the weights of smaller size. The fractions of the gramme should be tested in the same manner.

If the weights do not agree among themselves, some book on physico-chemical measurements should be consulted for further details. It may be necessary to send the weights to the maker for repairs.

In carrying out a gravimetric analysis it is not necessary that the weights should be of the exact value marked on them, but they must agree among themselves. But if they are to be used for standardising volumes they should be, at all events, nearly accurate. The measurement of volume is, however, not so accurate as that of weights, and sets of weights are rarely sufficiently inaccurate to affect the standardisation of volumes.

APPENDIX B

CALIBRATION OF FLASKS, PIPETTES AND BURETTES

It is not intended to give an exhaustive description of the methods of calibration. For such methods the student is referred to some book dealing with physico-chemical measurements. All that is attempted here is to enable the student to test whether his apparatus has the requisite degree of accuracy.

Apparatus is graduated in various ways. Since both the liquid and the containing glass expand, it makes a difference whether, for example, a litre flask contains 1,000 grammes of water at 4° C., or at 15° C. or at 17·5° C. It also makes a difference whether the weight is taken in air or *in vacuo*. The standard graduated flasks, verified and stamped at the Reichsanstalt, at Charlottenburg, in Germany, are marked on the basis of a litre of 1,000 grammes of water weighed *in vacuo* at 4° C. It makes a difference whether the flask is graduated to contain a litre or to allow a litre to be poured out from it. The Reichsanstalt standard is graduated in the latter way, no time being allowed for draining. Standard burettes and pipettes are graduated to deliver the given volume in a certain definite number of seconds. The pipettes, burettes and flasks used in one operation should be all graduated for the same temperature, and probably the most common is 17·5° C., which is approximately the average laboratory temperature, and litre flasks are more commonly graduated to contain 1,000 grammes of water weighed in air at that temperature. This is called the Mohr litre and is about 2·3 c.c. larger than the true litre. If all the measuring apparatus is made on this basis it is perfectly good for titrations. A litre flask constructed in this way after being thoroughly cleaned and dried by washing out with alcohol and afterwards with ether, which is removed by a blast of air, may be tested for accuracy in the following manner: Place the empty flask along with a kilogramme weight on one pan of the balance, counterpoise, remove the kilogramme weight and pour water into the flask till the counterpoise is just balanced. Any drops of water clinging to the neck of the flask should be removed by blotting paper. If, when the exact counterpoise is reached, the

water is at the level of the mark, the graduation is correct, otherwise the error should be determined. Smaller flasks are calibrated in a similar manner, the proper weight corresponding to the volume being employed.

Pipettes are used chiefly for delivering liquid, and the graduation will differ with the method of delivery. Probably the most satisfactory graduation of the amount in a given number of seconds, which will vary with the size of the pipette, the pipette being held vertical. A drop will in this case remain in the pipette. Sometimes the graduation is made on the supposition that this drop will be largely removed by touching the point of the pipette against the side of the vessel into which the liquid is delivered or the pipette is held against the side of the vessel during delivery. To test the accuracy of a pipette fill to the mark with water which is then run out into a tared vessel and weighed. One or two trials will determine which style of delivery is expected, and the accuracy of the graduation can be tested.

Burettes may be calibrated by running out into a tared flask successive quantities of 5 c.c. of water, weighing and tabulating the results.

If there is one accurate burette in the laboratory others can be readily compared with it and thus standardised by titrating equivalent solutions of alkali and acid against each other. Successive quantities of about 5 c.c. of alkali are run out from the burette whose accuracy is known and the amounts of acid necessary determined. If these agree with the quantities of alkali, the two burettes are alike, otherwise the discrepancies must be tabulated. Of course, the equivalency of the acid and alkali must have first of all been assured. This may be done by running out 50 c.c. of acid from a 50-c.c. pipette and adding to this acid 50 c.c. of the alkali from the same pipette. If the two solutions neutralise each other they are equivalent and the actual concentration is a matter of indifference.

APPENDIX C

ELECTROLYTIC DISSOCIATION AND THE MASS LAW

THE relation of general chemistry to analytical operations is well shown in the application of the theory of electrolytical dissociation and the law of mass action.

The combination of Boyle's law and Charles' law gives rise to the formula $pv = RT$ where p and v represent the pressure and volume of the molecular weight of any perfect gas and T its temperature measured from the absolute zero. When p is measured in grammes per square centimetre and v in cubic centimetres, the molecular weight in grammes and the temperature in centigrade degrees R has the value 84,760. In so far as any gas or vapour approaches the ideally perfect gas this formula holds and applies not only to hydrogen, oxygen and nitrogen, but to ammonia, hydrochloric acid, phosphorus, trichloride and other substances in the condition of vapour. But if the formula of ammonium chloride is taken as NH_4Cl, and the formula of phosphorus pentachloride as PCl_5, the value of R calculated for these substances when volatilised is nearly twice the normal. It is found, however, that the vapour formed by the volatilisation of ammonium chloride consists of a mixture of ammonia and hydrochloric acid, which can be separated from each other by diffiusion through unglazed porcelain. In the same way phosphorus pentachloride is broken up into phosphurus trichloride and chlorine. As the temperature is lowered recombination takes place and the original compounds are reformed. The decomposition just spoken of is called dissociation.

In 1877 Pfeffer, in the course of botanical experiments, found that when solutions of substances like cane sugar are placed in a porous cell whose pores are closed by a suitable membrane such as cupric ferrocyanide, and the cell is put into pure water, water is absorbed by the solution. By a proper arrangement of the apparatus he discovered that the absorption of water goes on till the pressure exerted reaches a limit. He found that this pressure varied as the concentration of the solution and was proportional to the absolute temperature.

Pfeffer's experiments were disregarded for a number of years, but in 1887 van't Hoff drew attention to them and showed

that the pressure, to which the name osmotic was given, was the same as would be exerted by the quantity of the solute in the gaseous condition (the volume being the same), and advanced the theory that substances in solution are practically gaseous. In fact for dilute solutions the formula $pv = RT$ was found to hold where R had the same meaning and the same value as in the case of gases.

But while sugar gave the normal value for R, salt and similar substances gave a higher value, and Arrhenius, in 1887, pointed out that the substances giving a high value for R are substances that can be electrolysed, and he suggested that just as ammonium chloride when volatilised gives a high value because it is dissociated, so substances in solution which give a high value are dissociated, and the dissociation was called electrolytic dissociation. According to the theory sodium chloride in solution dissociates into sodium and chlorine. The sodium cannot, however, be separated from the chlorine by diffusion as ammonia can be separated from hydrochloric acid by diffusion when ammonium chloride is volatilised; but when a current of electricity is passed through a solution of sodium chloride, sodium goes to the negative pole and chlorine to the positive; and though the solution of sodium chloride shows more of the properties of sodium or of chlorine, the substances which appear at the electrodes have the ordinary properties of the elements. According to the theory the dissociated constituents are ions each of which is charged, the sodium ion with positive electricity, the chlorine with negative. The charged ions do not have the ordinary properties of the elements, but when they reach the electrodes they are discharged and the usual characteristics appear.

Most of the operations which take place in analysis are due to the interaction of ions. When sodium chloride interacts with silver nitrate, the ions interchange; the silver ion goes with the chlorine ion and the sodium ion with the NO_3 ion. If sodium chloride solution is mixed with potassium nitrate, all of the ions remain in solution, and from the appearance merely it would be impossible to tell whether or not there is any interaction, but by special experiments it may be shown that an interaction does take place; and if a normal solution of sodium chloride be mixed with a normal solution of potassium nitrate, the mixture is in the same physical condition as if a normal solution of sodium nitrate were mixed with a normal solution of potassium chloride. But since silver chloride is nearly insoluble, when silver and chlorine come together they form a neutral body and do not separate, so that the mixture of silver ions and NO_3 ions with sodium ions and chlorine ions

gives rise to solid silver chloride, while the sodium ions and NO_3 ions are left in solution. The small quantity of silver chloride which is in solution exists mainly in the form of ions, but a minute fraction dissolves in the unionised condition.

According to the theory, the ions move about in all directions in the solution, now combining, now dissociating. If the number of silver ions is increased in any way, the chlorine ions more frequently come in contact with them, hence combination takes place to a greater extent and as only a certain quantity of unionised silver chloride can remain in solution, any unionised silver chloride that is formed is precipitated. In the same way an excess of chlorine ions will precipitate silver ions from solution. Silver ions may be added by addition of a solution of silver nitrate, and chlorine ions by the addition of sodium chloride.

If solutions are mixed in the proportion represented by the equation

$$AgNO_3 + NaCl = AgCl + NaNO_3,$$

it is found that if the silver chloride is filtered off, the clear filtrate can be rendered cloudy by the addition of either silver nitrate or sodium chloride.

The law of mass action states that if C_1 and C_2 are the concentrations of the ions, and C_3 the concentration of the unionised salt in solution, $\frac{C_1 \times C_2}{C_3} = K$, where K is a constant depending upon the nature of the substance. The value of C_3 is constant in the case above considered, it is the concentration of the unionised silver chloride in solution. Hence, if C_1 is increased, C_2 must correspondingly diminish, that is, if silver ions are increased in number the chlorine must correspondingly diminish. This means that chlorine is more completely precipitated from the solution by adding excess of silver nitrate. This is why excess of silver nitrate is added in precipitating a chloride, and the same principle applies to other precipitations.

Most soluble salts, if in not too concentrated solution, are largely dissociated, so also are what are called the strong acids and bases, such as hydrochloric and nitric acids and sodium and potassium hydroxide. But acids like acetic are not largely dissociated in the solutions of ordinary concentration, and the same is the case with ammonia. In fact, strong acids and bases are those which are largely dissociated, and weak acids and weak bases are those which are but slightly dissociated.

Though acetic acid is only slightly dissociated, sodium and potassium acetate in solution are largely dissociated. In the

same manner, though ammonium hydroxide is slightly dissociated, ammonium chloride, ammonium nitrate and ammonium sulphate are largely dissociated. In fact ammonium acetate, though formed from the weak base and the weak acid, is largely dissociated in solution.

Reasoning similar to that given above in the case of silver chloride may be used in connection with acetic acid. The slight ionisation of acetic acid can be still further diminished and the acid effect lessened by addition of the very soluble sodium or potassium acetate. Methyl orange is reddened by acetic acid, but the red colour can be removed by the addition of sodium acetate. In the same way phenol phthalein is turned red by the addition of ammonia, but the colour can be almost discharged by the addition of ammonium chloride or nitrate. In this experiment the solid salts should be added so that the solutions may be saturated.

When ammonia is added to a solution of magnesium sulphate or other salt of magnesium, a precipitate of magnesium hydroxide is formed. The presence of a large quantity of ammonium chloride in the solution prevents this precipitation, and according to the theory, this is due to the ammonium chloride preventing the dissociation of ammonium hydroxide, so that the latter can have no effect on the magnesium salt, since analytical reactions take place, mainly, if not entirely between ions. This explanation is slightly different from that given in the chapter upon the Determination of Magnesium, but the difference is rather in the form of expression than in essentials.

When an acid is sufficiently weak, its salts dissociate in a somewhat different manner, sodium carbonate dissociates into a free acid, which is weak, and a free base, which is strong. This involves the interaction of the salt with water, and the dissociation is called hydrolytic. As the sodium hydroxide produced is a strong base, sodium carbonate is in many of its reactions similar to caustic soda.

If the base is weak and the acid strong, the effect of the latter is predominant. Ferric chloride, for instance, when dissolved in water has an acid reaction.

Electrolytic dissociation plays an important part in the use of indicators for alkalimetry and acidimetry. For the most part, indicators are very weak acids or very weak bases. Phenol-phthalein, for example, is a very weak acid, and is very slightly dissociated. The undissociated compound is colourless. But when caustic soda or caustic potash is added, the sodium or potassium salt formed is dissociated. There is probably some intramolecular rearrangement which need not

concern us here, but the point of importance is that the anion produced is red. In the same way, when ammonium hydroxide is added to phenol-phthalein, the ammonium salt, being ionised, gives a red colour. But the salt formed by ammonia and phenol-phthalein is not so much dissociated as that formed by caustic soda or potash with phenol-phthalein, and if a large quantity of ammonium chloride is added, the dissociation may be made practically zero, that is, the colour is discharged and the presence of ammonia cannot be satisfactorily detected by phenol-phthalein as indicator. Any other method of lessening the dissociation has a similar effect, for instance, the addition of alcohol or acetone discharges the colour from phenol-phthalein which has been reddened by ammonia.

Methyl orange, on the other hand, is a weak base. When undissociated, the colour is yellow; when it forms salts with acids, the dissociation gives rise to a cation of the characteristic pink colour. Acetic acid is a sufficiently weak acid to yield a salt only slightly dissociated, and so the pink colour produced by the acetic acid can be changed to yellow by diminishing the dissociation. This can be done by the addition of acetates or of alcohol or other suitable organic liquids. Hence methyl-orange is not a suitable indicator for acetic acid. Carbonic, boric, and silicic acids are so weak that even in aqueous solution methyl orange does not form dissociable salts, and so they do not redden methyl orange. Sodium carbonate, therefore, acts with methyl orange just as caustic soda does. This was assumed to be the case in the description of processes of titration in the chapter on Alkalimetry.

APPENDIX D

ANALYTICAL FACTORS.

Given.	Desired.	Factor.	Logarithm.
$BaSO_4$ . .	Ba . . .	·5885	·7697
	BaO . .	·6570	·8176
	$BaCl_2$ . .	·8923	·9505
	$BaCl_2$, $2H_2O$.	1·0466	·0198
	S . . .	·1374	·1379
	SO_3 . .	·3430	·5353
	SO_4 . .	·4115	·6144
	H_2SO_4 . .	·4202	·6234
CaO . .	Ca . . .	·7146	·8541
	$CaCO_3$ . .	1·7847	·2516
	$CaSO_4$ . .	2·4280	·3853
$CaCO_3$ . .	Ca . . .	·4004	·6025
	CaO . .	·5603	·7484
	$CaSO_4$ . .	1·3605	·1337
$CaSO_4$ . .	Ca . . .	·2943	·4688
	CaO . .	·4119	·6147
	$CaCO_3$ . .	·7350	·8663
Cl . .	HCl . .	1·0284	·0122
	NaCl . .	1·6486	·2171
	KCl . .	2·1026	·3228
Cu_2S or CuO .	Cu . . .	·7989	·9025
Fe . .	FeO . .	1·2865	·1094
	Fe_2O_3 . .	1·4298	·1553
Fe_2O_3 . .	Fe . . .	·6994	·8447
$PbSO_4$ . .	Pb . . .	·6831	·8345
	PbO . .	·7359	·8668
	PbS . .	·7889	·8970
$PbCrO_4$ . .	Pb . . .	·6410	·8068
	PbO . .	·6905	·8392
	$PbSO_4$ . .	·9383	·9724

Given.	Desired.	Factor.	Logarithm.
$Mg_2P_2O_7$	Mg	·2184	·3392
	MgO	·3621	·5588
	P	·2787	·4452
	P_2O_5	·6379	·8048
SiO_2	Si	·4693	·6715
AgCl	Ag	·7526	·8766
	Cl	·2474	·3934
	HCl	·2544	·4055
	$AgNO_3$	1·1852	·0738
Sn	SnO_2	1·2689	·1034
SnO_2	Sn	·7881	·8966
Zn	ZnO	1·2448	·0951
	ZnS	1·4906	·1734
ZnO	Zn	·8034	·9049
ZnS	Zn	·6709	·8266

N.B.—The symbols in this table are used instead of the names. Properly speaking the amount of magnesium oxide got from $Mg_2P_2O_7$ is 2MgO, but for convenience it has been writtten MgO. Similarly in several other instances.

Logarithms.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts. 1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

Logarithms—*continued.*

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Anti-logarithms.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
·00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
·01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
·02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
·03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
·04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
·05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
·06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
·07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
·08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
·09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
·10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
·11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
·12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
·13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1 77	0	1	1	1	2	2	2	3	3
·14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
·15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
·16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
·17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
·18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
·19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
·20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
·21	1622	1626	1629	1633	1637	1641	1644	1648	165 2	1656	0	1	1	2	2	2	3	3	3
·22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
·23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
·24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
·25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
·26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
·27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
·28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
·29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
·30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
·31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
·32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
·33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
·34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
·35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
·36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
·37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
·38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
·39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
·40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
·41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
·42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
·43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
·44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
·45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
·46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
·47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
·48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
·49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Anti-logarithms—*continued.*

	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
·50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
·51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
·52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
·53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
·54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
·55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
·56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
·57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
·58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
·59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
·60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
·61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
·62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
·63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
·64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
·65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
·66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
·67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
·68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
·69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
·70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
·71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
·72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
·73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
·74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
·75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
·76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
·77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
·78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
·79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
·80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
·81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
·82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
·83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
·84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
·85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
·86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
·87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
·88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
·89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
·90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
·91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
·92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
·93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
·94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
·95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
·96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
·97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
·98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
·99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20